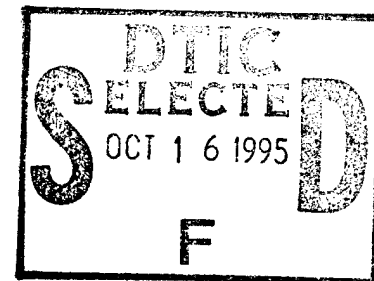


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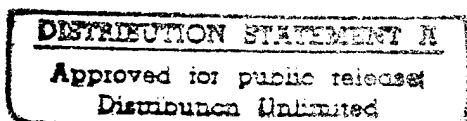


Single Crystal Growth of  
Potassium Titanyl Arsenate (KTA)  
for Nonlinear Optics

Roger F. Belt, John W. Ings,  
Mark H. Randles and Thomas E. Iradi, Sr.

Contract N00014-90-C-0238

September 1990 - October 1993



Airtron Division  
Litton Systems Inc.  
200 E. Hanover Avenue  
Morris Plains, NJ 07950

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53570 Silvergate Avenue, Room 2070  
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## Abstract

This program was directed to the single crystal growth of the nonlinear optical material potassium titanyl arsenate,  $\text{KTiOAsO}_4$ . This crystal is useful for nonlinear parametric processes to generate tunable laser frequencies. Our growth method was chosen to be hydrothermal. The solubility and phase relations were investigated for selected K/As ratios in  $\text{KH}_2\text{AsO}_4$ -KOH solutions over a temperature range of 300-600°C and 10,000-30,000 psi. All initial data were obtained with 0.20 inch diameter x 2.50 inch long platinum capsules in Tempress type autoclaves. The most favorable results were repeated in Morey type autoclaves of 0.875 inch diameter. The P-V-T data were generated and extrapolated for use in gold liners and Rene' 41 autoclaves with a pressure balancing method. All data were transferred to 1.5 inch diameter x 18 inch long autoclaves with gold liners. For the latter system, both nutrient and larger seed crystals were grown from a  $\text{K}_2\text{WO}_4$ - $\text{LiWO}_4$  flux. The internal and external degrees of fill were adjusted to obtain a near balance at a pressure of 25,000 psi and a temperature of 560-590°C. Growth runs were made for 7-10 weeks under a growth gradient of 30°C with a 10 molar  $\text{KH}_2\text{AsO}_4$  mineralizer. Spontaneously nucleated seeds were employed initially while later runs utilized (011) cut and polished seeds. We have grown crystals of { 18 x 18 x 35 } mm<sup>3</sup> at rates of up to 1mm/side/week. The crystals were single domain, high internal quality, and water white. A final production process was developed, crystals were tested in different OPO applications and results reported in several papers.

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## 1.0 Introduction

Potassium titanyl arsenate ( $\text{KTiOAsO}_4 = \text{KTA}$ ) is one member of a class of nonlinear optical materials which have become extremely valuable in present laser technology. A good description of the many structures, properties, growth, and applications has been compiled in a recent review<sup>1</sup>. It can be seen readily that favorable nonlinear crystals possess the following attributes. They have large effective nonlinear coefficients, excellent optical transmission from the ultraviolet through the infrared regions, good physical and mechanical properties, non hygroscopic, and can be grown in high quality single crystals with high resistance to optical damage. Many of the problems associated with nonlinear materials are connected with synthesis, growth, and availability to the laser community. At the beginning of our program, only one favorable crystal, namely  $\text{KTiOPO}_4$ , KTP, was commercially grown and exploited<sup>2</sup>. This crystal has a few disadvantages for use as a parametric oscillator.

Nonlinear materials are valued now for optical parametric processes, i.e., as tunable laser sources. Most of the original research was performed in this area over 20 years ago. However, the available crystals at that time were quite susceptible to optical damage and the devices were only operable at very low power. Much of the history and applications are now described in contemporary books on nonlinear optics.<sup>3</sup> The latter also gives new device results but some still do not exploit the recent guided wave devices.<sup>4</sup> These may become significant for low cost, fixed frequency, miniature sources for lasers. The parametric process in a good nonlinear crystal can yield significant power over a wide range of the spectrum including the 1-5  $\mu\text{m}$  infrared. This region is valuable for military countermeasures, environmental monitoring of gaseous pollutants and medical technology. Ideally, crystals are desirable for accessing more of the infrared. The nonlinear titanyl compounds offer a path to this goal because they are fundamentally insulators rather than semiconductors. Thus they have the most potential like the borates for good damage resistance.

The first crystals of KTA were grown in 1989 by means of a  $\text{WO}_3$  flux solution<sup>5</sup>. At that time, it was shown from measured physical properties to have a higher nonlinear coefficient and extended transparency in the infrared compared to KTP. The  $\text{WO}_3$  flux is not the best because of fairly large amounts of impurity inclusions which limit damage resistance. It was reported in later papers<sup>6,7</sup>, that the  $\text{K}_6\text{As}_4\text{O}_{13}$  type fluxes could be used also to grow KTA with high purity. An alternate method to grow KTA is the hydrothermal technique. A synthesis was reported in 1990 which yielded crystals of 1-2mm size<sup>8</sup>. Thus since KTA is incongruently melting, i.e., it decomposes near the melting point, a crystal grower must use a solution process to crystallize material far below the decomposition temperature. At the inception of our program in 1990, the whole status of growth was problematic. Only the  $\text{WO}_3$  flux was available. However, the hydrothermal method was feasible and gave superior results with KTP. Thus our program was initiated and most likely to give high quality crystals. Furthermore, all of the equipment used for KTP growth was

available for KTA growth. Thus no separate capital equipment investment was necessary. One other major problem was the concern for personal and environmental safety. The presence of arsenic in KTA dictates that all work be done most carefully in closed growth systems and isolated areas. The hydrothermal growth is totally sealed and does not emit to the atmosphere except in a rare case of autoclave failure. Airtron already possessed isolated rooms and facilities for working with arsenic compounds. It should be noted that KTA in single crystal form is totally insoluble in water or any other common solvent. Thus it is extremely stable in optical devices.

For those unfamiliar with crystal growth, the hydrothermal method is a solution growth process carried out under high temperature and pressure. With these extreme conditions, a normally insoluble compound like KTA can be dissolved in a water-mineralizer solution and subsequently transported to a seed. Thus under controlled conditions, growth of the seed can occur to give a sizeable final product. High quality material is obtained because growth occurs slowly under a relatively low thermal gradient. Like any other growth method, the hydrothermal method is not free of problems; seed crystals must be available, a ready supply of nutrient must be produced, mineralizers and solubility relations have to be investigated, satisfactory growth conditions of temperature, pressure and gradients have to be finalized. Usually these data are determined from runs in small autoclaves of 0.38 inch diameter x 6.0 inch lengths. A scale up to autoclave sizes of 1.5 inch diameter x 18 inch length can then produce crystals of 1-1.5 inch dimensions. The following sections relate the details of our growth studies on KTA whereby crystals were grown and a process developed for attaining high quality finished products.

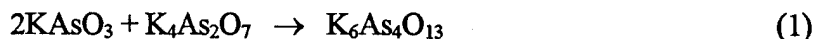
## 2.0 Material Preparation

The preparation of chemical materials for any commercial process is generally dependent upon availability, price, and purity. There may be more than one possible technique to prepare the necessary compounds. For  $\text{KTiOAsO}_4$ , the primary elemental constituents are sources of K, Ti, and As.

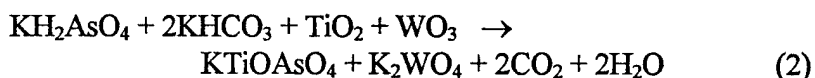
### 2.1 Starting Chemicals

The normal source of K was always in the form of  $\text{K}_2\text{CO}_3$  which was purchased as 99.9+ % purity. The thermal degradation of  $\text{K}_2\text{CO}_3$  leads to  $\text{K}_2\text{O} + \text{CO}_2$  at temperatures above 500-600°. The source of Ti was in the form of powdered  $\text{TiO}_2$  of at least 99.99% purity. This material was available from several sources. The largest impurity is Fe in an amount of 10-50 ppm. The As is available as  $\text{As}_2\text{O}_5$  in powdered form. It is also lightly hygroscopic and somewhat volatile at high temperatures.

At various times, small single crystals were prepared from  $\text{WO}_3$  or  $\text{MoO}_3$  fluxes. These fluxes were specifically  $\text{Li}_2\text{WO}_4$ ,  $\text{Li}_2\text{MoO}_4$ , the analogous potassium salts or a mixture of the two. The compounds were purchased from ordinary supply houses with a purity of 99.9%. In cases later in the program where KTA was obtained from a so-called self flux of composition  $\text{K}_6\text{As}_4\text{O}_{13}$ , the latter was prepared by mixing  $\text{KAsO}_3$  and  $\text{K}_4\text{As}_2\text{O}_7$  as in the equation (1)



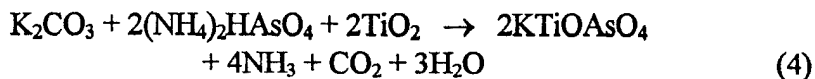
KTA can also be crystallized from a mixture of the following in equation (2)



At various times where KTA is prepared from the  $\text{KH}_2\text{AsO}_4$ , the latter can be prepared by dissolution of  $\text{K}_2\text{CO}_3$  and  $\text{As}_2\text{O}_5$  in boiling water via equation (3)



Several routes exist for the synthesis of KTA in powdered polycrystalline form. This KTA may be used subsequently for nutrient, flux growth or sintering. The material is always free of most contaminants since the other products are volatile gaseous compounds. In hydrothermal growth performed in water, the water always serves as part of the solvent. A group of French investigators prepared<sup>9</sup> KTA by means of equation (4)



At Airtron we prepared KTA via a simple reaction of equation (5)



## 2.2 Seed Crystals

Seed crystals are required for several reasons in our program. Broadly they are required for either growth or dissolution studies and must consist of small single crystals of KTA which can be attached to the interior of the autoclave liner by means of a fine gold wire. At the beginning of our investigations where mineralizers and solubility were of prime concern, the source of the seed crystal was always from flux grown KTA via the  $\text{MoO}_3$  route. Some of these are pictured in Figure 1(a).

The seeds were normally 2-4 mm in size, of random orientation, and had trace levels of 100-500 ppm of residual Mo. Further into our program when larger seeds were required for growth, these were also obtained from the  $\text{MoO}_3$  or  $\text{WO}_3$  flux process. However, the seeds were now larger with well developed faces and of specific orientation. Figure 1(b) gives an example which shows growth on a (201) oriented KTA seed of nearly 1 cm size. It should be mentioned that all of our flux grown KTA originated from E. I. DuPont Research Laboratories in Wilmington, DE. During the last half year of our effort, KTA crystals of a size 10-15 mm and grown from the  $\text{K}_6\text{As}_4\text{O}_{13}$  flux, became available. These were used as seeds in the crystal growth performed in 1.5 inch diameter autoclaves. The seeds were of precise orientation and cut from large flux grown boules. All of these seeds were polished on the growth faces and had a small hole drilled at one end where a gold wire passed through to hold the seed to the ladder.

## 2.3 Nutrient

In hydrothermal growth, nutrient refers to the source material of the KTA which is put into solution first and then transported to the seed for subsequent growth. It is highly important that one can obtain nutrient of high chemical purity, satisfactory physical size, and from a reproducible low cost preparation process. Chemical purity is necessary to grow a high quality crystal with excellent optical damage resistance. The physical size is important to obtain uniform growth. Particles which are 10-50 $\mu\text{m}$  or smaller tend to form a sludge at the autoclave bottom and greatly inhibit normal dissolution. Small crystals in a size range of about 0.1-1.0 mm are ideal since the solvent can freely circulate about the particle and dissolve it. A low cost, one step preparation of crystallites is very desirable to prepare kilogram batches of KTA for nutrient. One run may consume 100-200 g of nutrient in a 1.5 inch diameter autoclave.

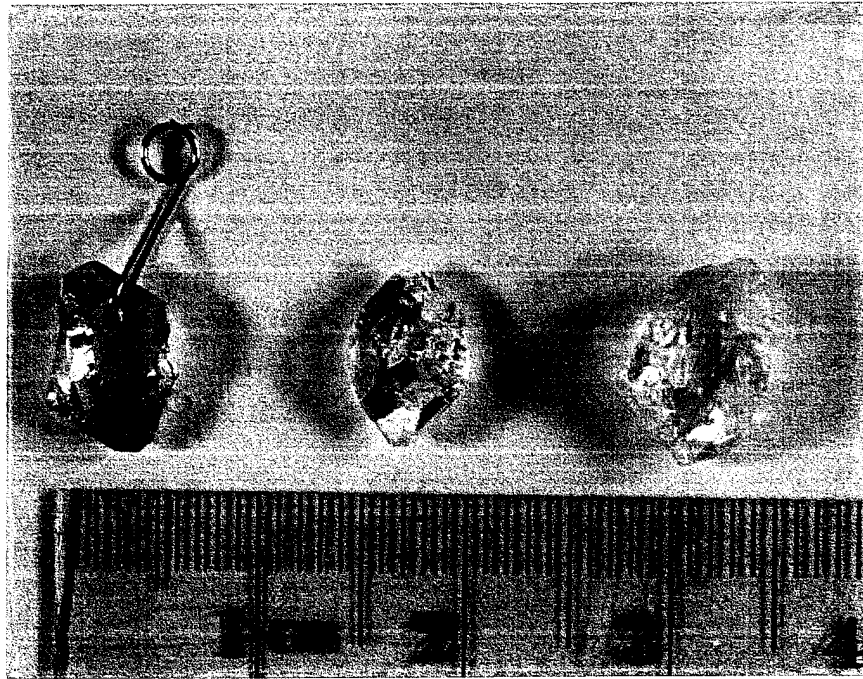


Figure 1 (a) Unoriented flux grown KTA seeds

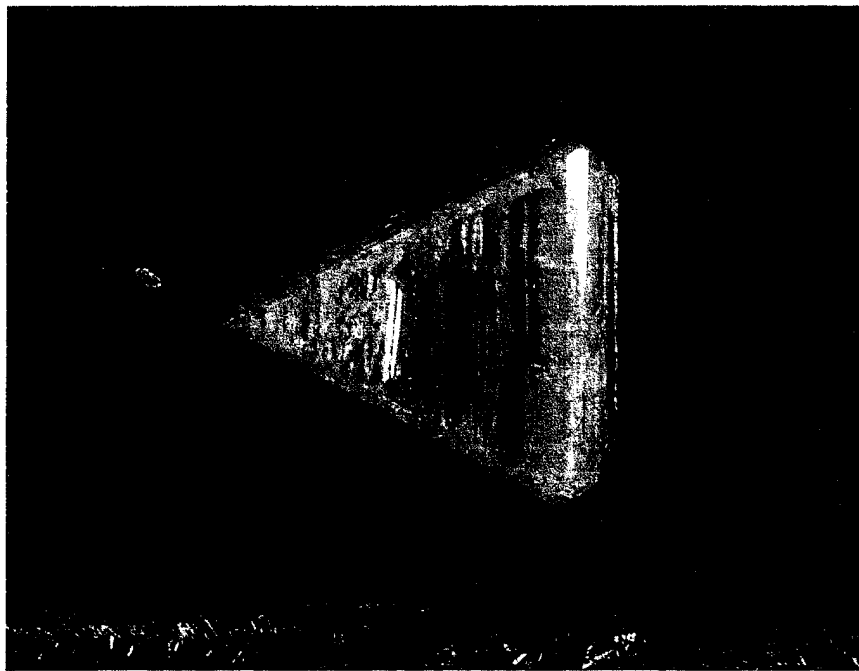


Figure 1 (b) KTA growth on (201) oriented flux grown KTA seed

Various sources of nutrient were employed at different periods during our program. Mainly this was a result of availability, i.e., from either a source outside of Airtron or from our own development. It is fitting at this stage to review the several types of nutrient we used along with some of their advantages or disadvantages. For reference, we list in Table I a summary of nutrient sources. While the best material appears to be crystals grown from a  $K_6As_4O_{13}$  flux, it can be seen that this requires a fairly large investment in platinum ware; thus it is relatively expensive for a production process. Finally we did a fair amount of research on sintered pellets which are potentially very low cost. More of this will be described later since some details need to be perfected. All flux growing for nutrient must be performed in platinum or gold crucibles. The precious metal use is unavoidable and contributes to costs. Very little of the metal is lost, usually 1-3% by weight, but metal inventory requires capital. Metal leasing is available, but of course these costs are passed along. When many autoclaves are used, a fair amount of KTA spontaneous nucleation occurs. This nutrient material is recycled and can even be combined with KTA from other sources.

Most of the nutrient supply in the early part of our program was obtained from the DuPont group in the form of small crystals as shown in Figure 1(a). These were prepared from a composition of mixed tungstates as given in Table II. Materials were placed in a platinum crucible and melted together at 1050°C. The inset at the bottom of the page shows the cooling schedule for crystallization. The crystals were separated by dissolving the flux with hot water. The tungsten content of the crystals was variable but in the range of 500-2000 ppm.

#### 2.4 Flux Crystals

The preparation of flux grown KTA was an important source of nutrient, small seeds, and in fact can be developed as a separate growth method. In this short section we present enough detail on flux growth of KTA so the reader can understand how these crystals are prepared and then used in the hydrothermal process.

The first reported crystallization of KTA was performed by Brahimi and Durand<sup>9</sup>. They combined equimolar mixtures of  $TiO_2$ ,  $KH_2AsO_4$ , and  $KHCO_3$  and heated them in a quartz tube for 12 hours at 400°C to begin reaction. The mixture was then heated to 700°C gradually and held for 48 hours. By slow cooling at a rate of 10 degrees/hour back to 400°C, small crystals of 0.1 mm size were obtained. These were quite suitable for X-ray structure determination and nonlinear optical studies via the powder method of Kurtz and Perry<sup>10</sup>. The KTA crystals were separated from the remaining flux by washing with hot water.

Table I

## Nutrient Sources for KTA Growth

Material Source of KTA	Preparation Technique	Physical State	Advantages	Disadvantages
Flux crystallization	from $\text{MoO}_3$ or $\text{WO}_3$	1-3mm crystals	easy, available, size, yield	cost, residual impurity, Pt container required, safety
Flux crystallization	from $\text{K}_6\text{As}_4\text{O}_{13}$	1-10mm crystals	size, yield, purity, orientation	growth rate, safety, Pt required, large $\Delta T$
Spontaneous Nucleation (SN) crystals	from any hydrothermal growth run	0.1-2mm crystals	purity, size, reuse	cost, use of Au liners, low yields
Sintered pellets	sintered powders at $\sim 1000^\circ\text{C}$	1-5 mm pieces	purity, low cost, size	stability, uniform dissolution



Table II

Early Method for Flux Growth of KTA Nutrient

Melt Composition	Molar
$\text{KH}_2\text{AsO}_4$	1.50
$\text{K}_2\text{WO}_4$	0.90
$\text{LiWO}_4$	0.30
$\text{TiO}_2$	1.50

Temperature Profile:

Heat to 1050°C and cook  
 Ramp down to 980° at 3° / hr  
 Ramp down to 800° at 1° / hr  
 Pour out flux and slow cool crucible in furnace

When the linear and nonlinear optical properties of KTA were reported by DuPont in 1989, their crystals were grown from a  $\text{WO}_3$  flux<sup>5</sup>. Specifically, mixtures of  $\text{KH}_2\text{AsO}_4$ ,  $\text{KHCO}_3$ ,  $\text{TiO}_2$ , and  $\text{WO}_3$  were placed in platinum crucibles and heated to  $1000^\circ\text{C}$  for 10 hours. By slow cooling to  $750^\circ\text{C}$  at a rate of  $1^\circ\text{C}/\text{hour}$ , then overnight cooling to  $25^\circ\text{C}$ , crystals of 5-15 mm were obtained. They were separated from the flux by leaching with hot water. Slightly yellow colors were observed. In a subsequent paper<sup>11</sup>, the method was developed further to yield crystals of 2-5 cm size, inclusion free, and colorless. Both the  $\text{WO}_3$  and  $\text{MoO}_3$  fluxes were employed. Growth rates of up to 1 mm/day on major faces were attained. However, nearly 0.1-0.2% of Mo or W is still found in the crystals.

The group at Crystal Associates has developed methods for growing KTA and other isomorphs from flux solutions using vessels with up to 10 liter volume<sup>11</sup>. Basically their procedures follow those for KTP where the most success has been achieved with flux compositions of  $\text{K}_6\text{P}_4\text{O}_{13}$ . These are prepared from mixtures of the phosphates corresponding to  $2\text{KPO}_3$  and  $\text{K}_4\text{P}_2\text{O}_7$ . Similar solvents are useful for growing KTA or CTA. The basic method has been refined to grow crystals of cm size<sup>12</sup>. A seeded solution method is employed whereby saturated solutions are prepared at  $1000^\circ\text{C}$  and then slow cooled to  $850^\circ\text{C}$  to obtain growth. Controlled slow cooling at rates of  $2\text{-}5^\circ\text{C}/\text{day}$  is performed by a judicious use of heat exchangers. A recent application has been the growth of CTA<sup>13</sup>. We also mention this flux growth for two additional reasons. First, all of it was concurrent with our hydrothermal growth. Secondly, late in our program we were able to obtain a few seeds of KTA. These were used to grow KTA hydrothermally. An obvious advantage was that they were completely free of any W or Mo impurity from those respective fluxes as used originally by the DuPont group. Once the pure seeds are used in our hydrothermal method, the process is self sustaining and any impurities cease to be a problem.

## 2.5 Phase Studies

By phase studies or relations we can investigate what compounds are present under various conditions of temperature, pressure, and concentration of reactants. In hydrothermal systems it is necessary obviously to know under what conditions one can crystallize and grow the desired compound. For our situation in the growth of KTA, this is normally performed by heating the preferred chemicals in a closed autoclave, maintaining the conditions for a sufficient period of time, and then quenching the system back to normal pressure and temperature. The autoclave contents are then examined by X-ray diffraction to verify the identity of all solid phases; the normal liquid phase of pure water is removed by drying at  $100^\circ\text{C}$  or below.

It was of primary interest to us that the main components of KTA be used in any phase studies. Thus the following chemicals are important in our hydrothermal process. We used  $\text{H}_2\text{O}$ ,  $\text{KOH}$ ,  $\text{KH}_2\text{AsO}_4$ ,  $\text{K}_2\text{HAsO}_4$ ,  $\text{TiO}_2$ ,  $\text{As}_2\text{O}_5$ , and synthesized

KTiOAsO<sub>4</sub>. All of these were in the form of reagent grade chemicals of polycrystalline type with a purity of 99.9+%. The water was liquid and KOH was obtained from reagent grade pellets and added in the form of a solution.

The main results of a phase study can be presented in a so-called phase diagram. For example, in Figure 2 we show the results of Gier<sup>14</sup> for the ternary system of K<sub>2</sub>O-TiO<sub>2</sub>-As<sub>2</sub>O<sub>5</sub> at normal pressure. The figure shows the composition regime, enclosed by JKL, where the major phase of KTiOAsO<sub>4</sub> is stable. Compositions are given on the diagram in mole %. For hydrothermal growth it is expedient to obtain good mineralizers, i.e., those substances which can be added to pure water to greatly increase the solubility of KTP. Figure 3 shows such a diagram from Gier<sup>15</sup> who investigated data for KTA. The region ABCD encloses the preferred compositions. Notice that these are mainly dependent on the K/As ratio and can be obtained through the use of many different compounds of K and As. Use of these data assisted us in our growth program.

Of course hydrothermal growth of KTA was carried out in the presence of water at high temperature and pressure. For this reason phase studies are important to understand solubility in a qualitative fashion. For example, Figure 4 shows a phase diagram for KTP obtained by Laudise<sup>16</sup> under the conditions of 10 kpsi at 500-600°C.

While the KTA system is not identical, it is analogous and indicated that KTA could be crystallized from a variety of mineralizers at varying K/As ratios. The quantitative values of KTA solubility and the relative growth rates are not obtainable from phase diagrams. We discuss solubility more thoroughly for KTA in Section 4.0. Our results and those of other workers are compared for identical mineralizers and experimental conditions.

## 2.6 Safety Precautions

All of the arsenic containing compounds used in our program are considered toxic. Poisoning in small amounts can be quite abrupt with acute symptoms which can lead to shock and eventual death<sup>17,18</sup>. For this reason, a safe work area and careful planning are necessary. At Airtron an isolated room was constructed which contained an enclosed hood with an exhaust system always under positive pressure. Air was circulated through the hood and then captured by a fine HEPA filter system to trap any particulate matter and prevent it from exiting the building. Most of the arsenic compounds were fine powders and preparations were always performed in the hood by a properly clothed and masked technical person. Most weighings were also done in the hood. Routine blood tests are performed on each person who handles arsenic.

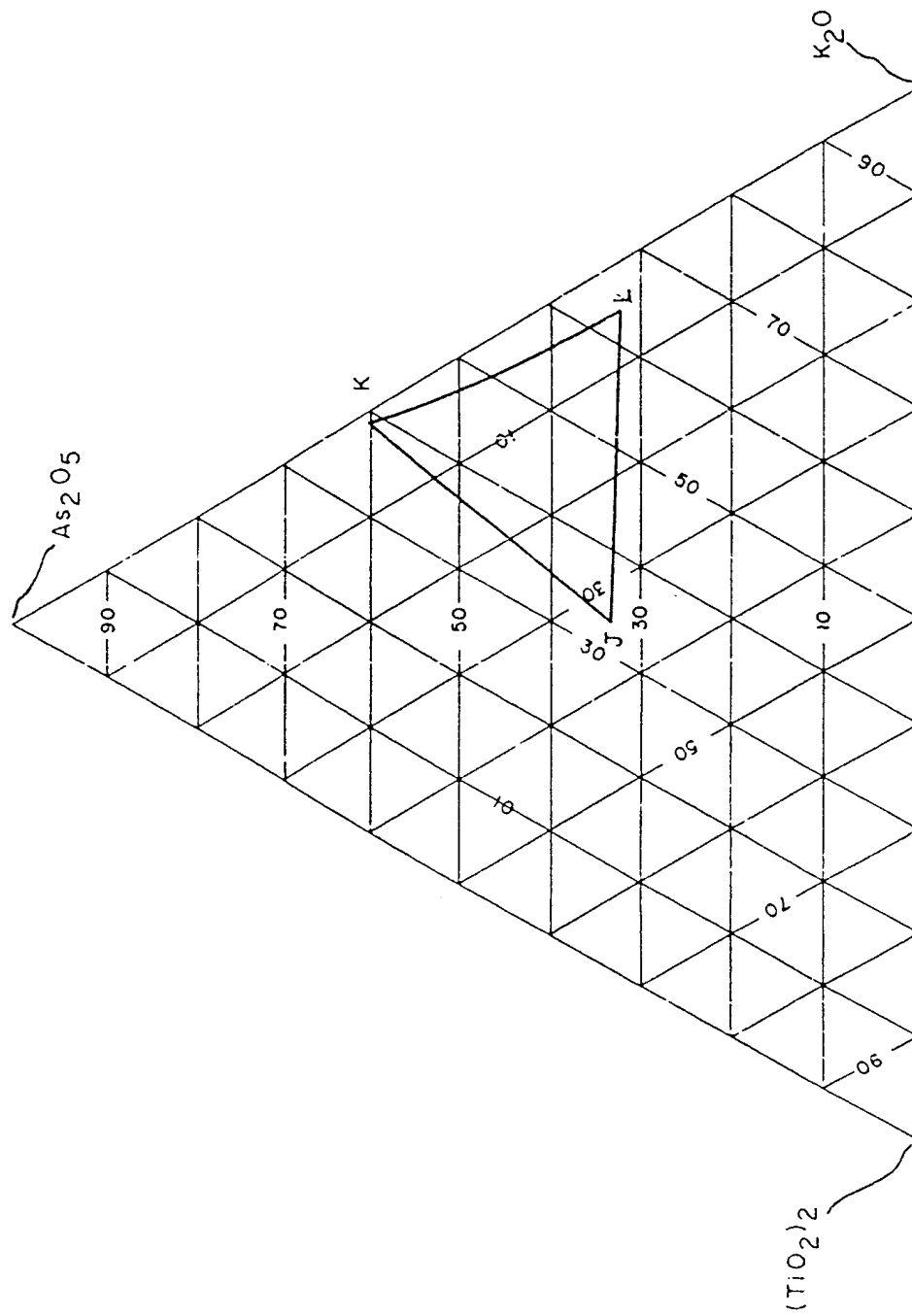


Figure 2 Phase diagram of the  $\text{K}_2\text{O}-\text{TiO}_2-\text{As}_2\text{O}_5$  system <sup>14</sup>

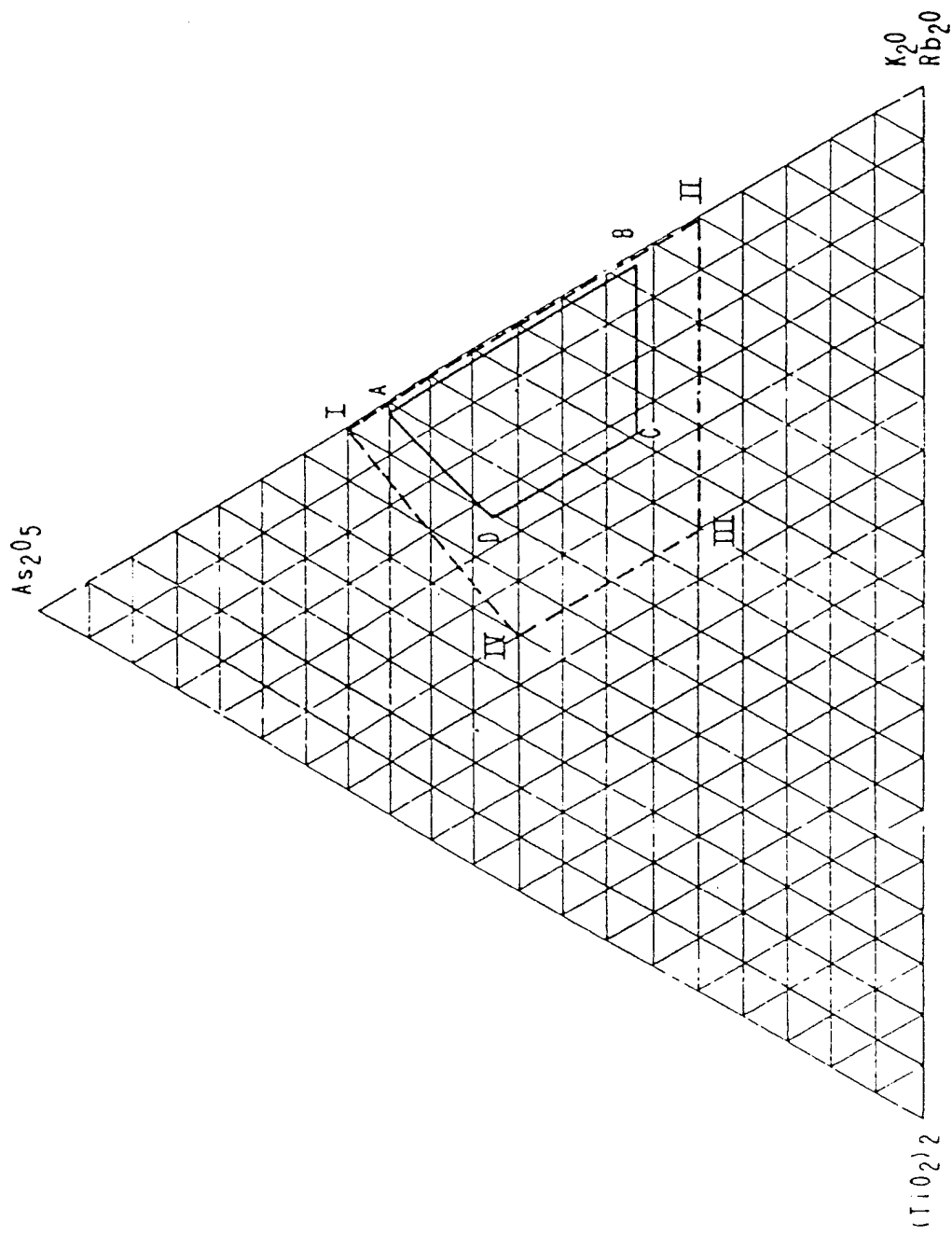


Figure 3 Phase diagram of glassy mineralizers useful for KTA growth <sup>15</sup>

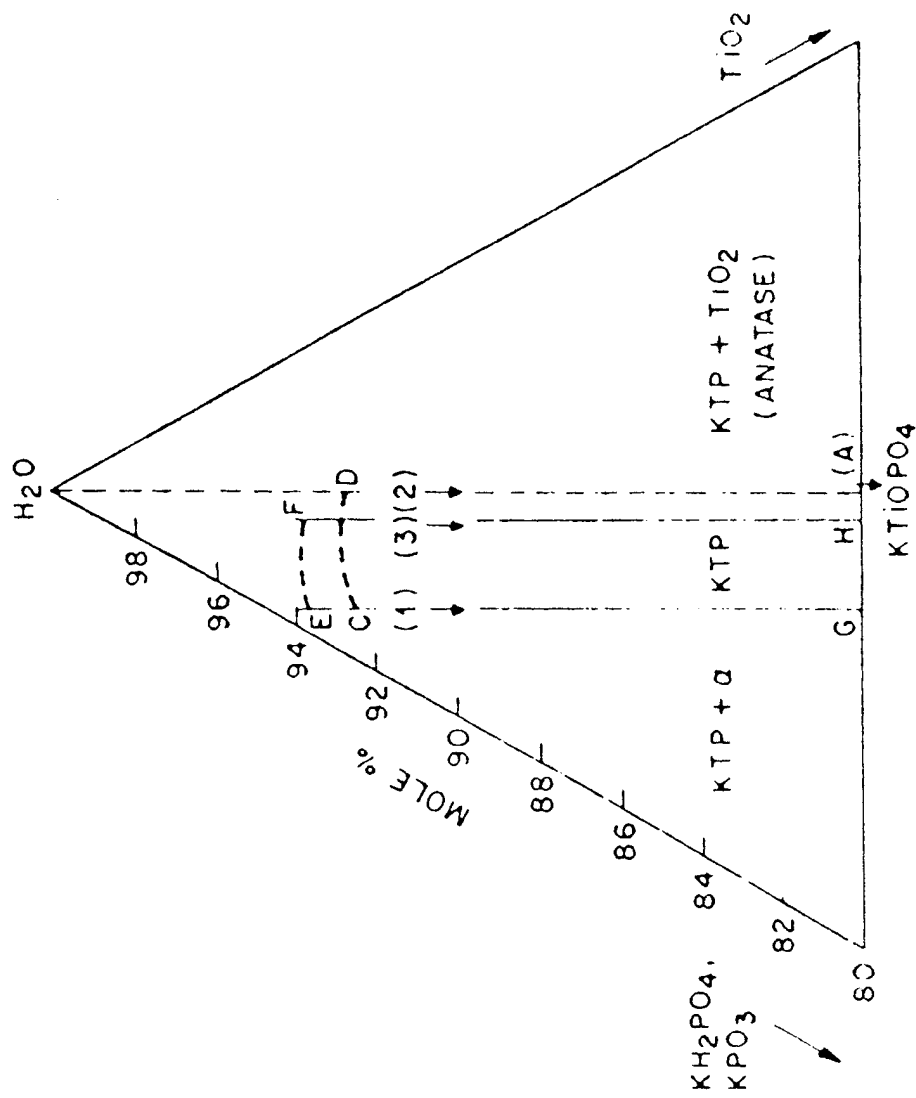


Figure 4 Schematic of the  $\text{H}_2\text{O}$  rich part of the  $\text{KPO}_3$ - $\text{TiO}_2$ - $\text{H}_2\text{O}$  system in 1m  $\text{K}_2\text{HPO}_4$  at 10kpsi and 500-600°C <sup>16</sup>

After materials were weighed, formulated, and mixed they were retained in closed jars until used in a crystal growth operation. Most of the crystal growing was performed in sealed systems. Thus, there was no problem unless a crucible or autoclave leaked. Fortunately we have never suffered a total mishap. However, it was prepared for by isolating an entire furnace or autoclave from normal production. With a furnace in operation and heating arsenic compounds, an exhaust hood and filter were always employed. Hydrothermal growth took place in an isolated cylindrical pit which was always covered by a steel safety hood and exhaust system. We have never experienced an explosive type autoclave rupture.

During the program, we have also investigated a large group of sintered compositions. The aim of these was for a low cost nutrient source. The many compositions were prepared as mixed powders which were pelletized and sintered. These were done in closed platinum crucibles at temperatures low enough to forestall any vapor emission.

The question may arise as to the proper disposal of any arsenic compounds which are used, discarded, or considered waste. Airtron has had a wealth of experience in this matter from its commercial GaAs operation. First of all we must distinguish between water insoluble and water soluble at 25°C. The former are collected as used in appropriate containers. The latter must be prevented from entering the waste water which may have a disposal plant or tributary for a final destination. Water soluble arsenic is oxidized first completely to  $\text{As}^{5+}$ . The  $\text{As}^{5+}$  as  $\text{AsO}_4^{3-}$  is then precipitated with  $\text{Ca(OH)}_2$  to yield the highly insoluble salt of  $\text{Ca}_3(\text{AsO}_4)_2$ . This compound can then be precipitated and filtered from solution to yield arsenic-free water. The  $\text{Ca}_3(\text{AsO}_4)_2$  can be combined with other water insoluble compounds. These are disposed of through an EPA approved carrier to an appropriate poison compound site.

It should be noted that single crystal KTA itself is a highly insoluble arsenic containing compound. As such it should be treated with respect and not ever ingested. However, it can be handled, cut, processed, coated, and used without harm. Adequate precautions must be taken for powdered KTA at all times. The single crystal can be disposed of through channels accessible to the GaAs semiconductor handler.

### 3.0 Autoclave Instrumentation

The principal tool for hydrothermal crystal growth is an autoclave. This is simply a steel vessel which can be heated to 600°C without rupture under an internal pressure of up to 30000 psi. This pressure is generated by the supercritical properties of water which basically acts as the solvent for KTA. In this section we describe all the autoclaves and their appurtenances we have used to grow crystals. Some fundamental information on hydrothermal growth is given in available references which also describe equipment<sup>19,20</sup>.

#### 3.1 Autoclaves

Autoclaves are constructed from high grade specialty steels whose physical properties have been measured thoroughly at elevated temperatures and pressures. The design of safe pressure vessels is a well developed art requiring cooperation between steel metallurgists and vessel engineers. Some of this art has been described in a monograph<sup>21</sup> for moderate conditions. Unfortunately some of the best technology has been available only at a few laboratories such as AT&T or E.I. DuPont. Special companies like Tempress at State College, PA or Autoclave Engineers at Erie, PA have a wealth of experience in design. The basic steels we have used for autoclave construction are cold rolled steel which is serviceable up to about 350°C at 30000 psi; for most common work the A-286 steel can be used in the range of 350-450°C at 30000 psi. Finally we have made extensive use of the Rene' 41 type alloys which can be operated at 450-600°C and 25000 psi. The life of a vessel is mainly governed by eventual creep caused by the extreme conditions. Hydrothermal growth runs may last from 500-1000 hours. The normal operating life of an autoclave will be in the range of  $10^4$ - $10^5$  hours. At this time the vessel may experience leaks due to protracted expansion and it should be scrapped. Internal cavity and external diameter measurements can be made after each run to follow the progress of creep in an autoclave. Logs are kept for each vessel.

Small autoclaves with internal volumes of 5-50 cm<sup>3</sup> are handy to perform phase studies, solubility of materials, and general P-V-T relations in any new chemical system. We have constructed and used two types whose internal volumes were about 15-20 cm<sup>3</sup>. The first of these was of Tuttle design<sup>22</sup> which is a vessel with a cold can seat closure. A diagram of this construction is given in Figure 5 as prepared by Tempress Inc. and used in their multi-unit research system pictured in Figure 6. The figure shows four stations with controls. The autoclaves themselves are at the top and not visible since they are surrounded by the furnaces and insulation. Henceforth, in this report we simply refer to this as the Tempress unit.

The Tempress autoclave system is a research apparatus suitable for preliminary hydrothermal investigations. The system is composed of four individual autoclaves



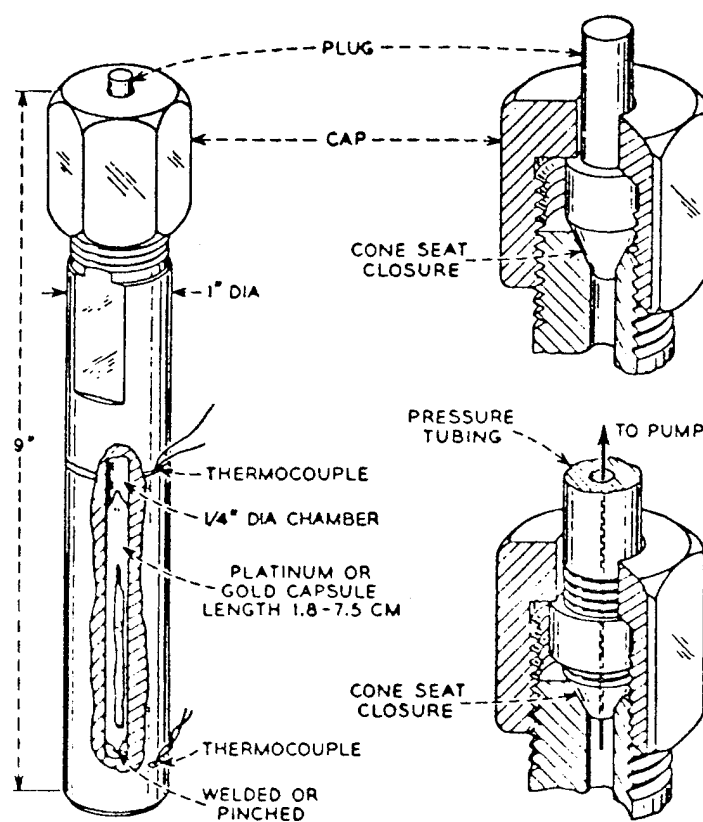


Figure 5

Reaction vessel with a cold-cone seat closure, Tempres Inc., State College, PA

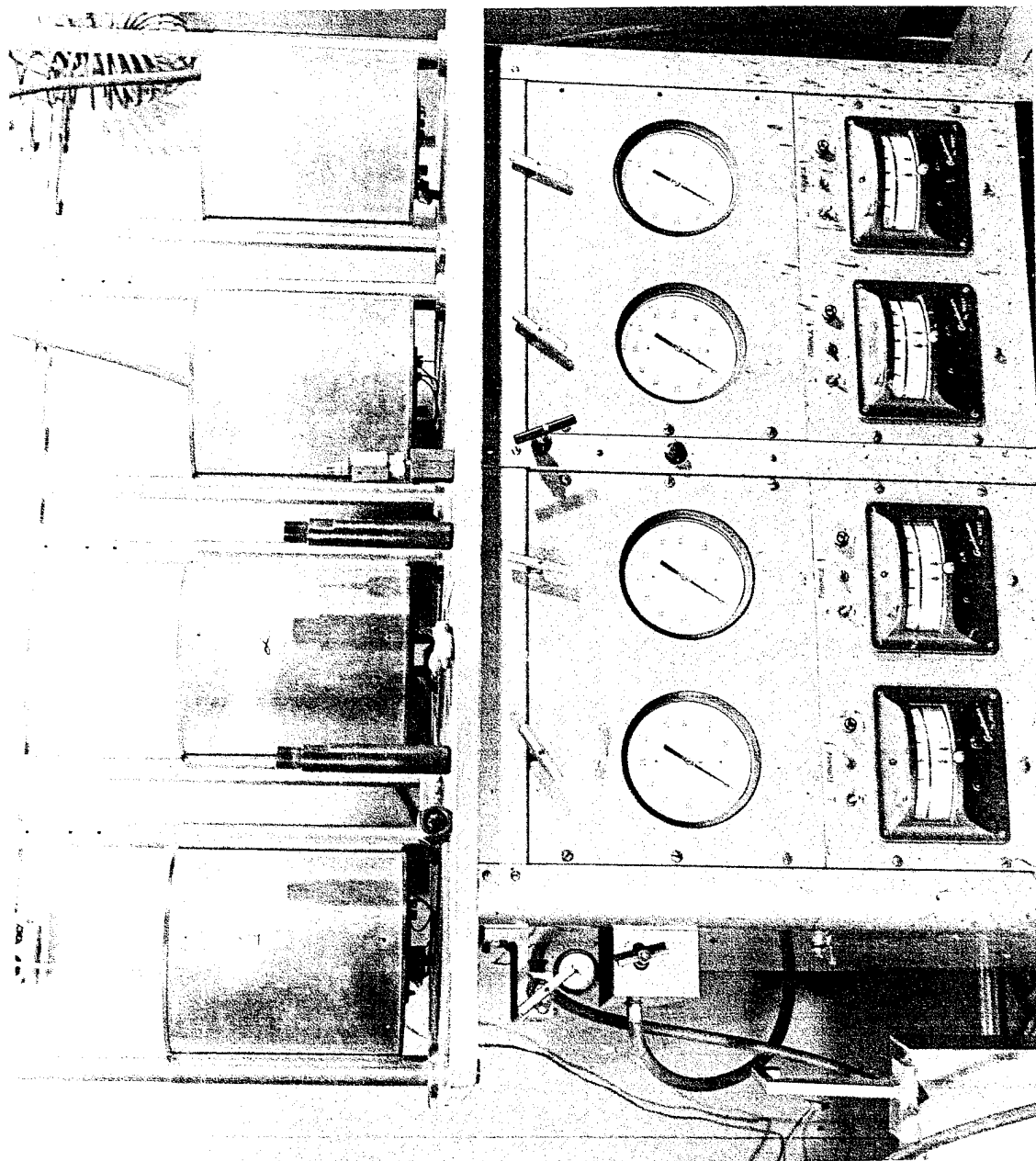


Figure 6      Tempress equipment for hydrothermal studies

prepared of stellite containers with each measuring 3/8 inch internal diameter and 7 inches long. Each autoclave station can be individually heated and pressurized by a hydraulic water pump, tubing, valves and gauges. The stellite autoclaves allow maximum operating conditions of about 750°C and 40000 psi. In order to protect the autoclaves from reactive chemicals (1/4 x 3) inch liner capsules of Ag, Au, or Pt are fabricated from tubing, sealed, and inserted in the stellite cavity. After each run the capsules are removed, cut open, and contents examined by weight, microscope, x-ray diffraction, or other chemical and physical tests.

We used these small autoclaves on the KTA program for the following main studies. (1) An examination of solvents, mineralizers, compositions, and phase relations at elevated temperatures and pressures. Some of these data were already known as a result of previous DuPont work but new areas were worth investigating. (2) A further study of other possible flux systems which may dissolve KTA without thermal decomposition or phase change. (3) The solubility of KTA as a function of temperature in currently used solvents and mineralizers. This work is best done on small single crystals by the weight loss method. (4) The rapid evaluation of chemical purity of starting materials, crystal quality, and reactivity of components toward metal liners before proceeding with larger and more expensive autoclaves. (5) Safety considerations in future KTA work. All unknown experiments should be attempted first in small autoclaves because of cost and safety.

We also constructed two small Morey-type closure<sup>23</sup> vessels from Rene' 41 alloys. These vessels have a gasket closure composed of a noble metal which is readily pliable. A schematic of this autoclave is given in Figure 7. The nature of the seal limits the operating conditions to about 500°C and 10000 psi. However, valid extrapolations can be made to higher temperatures since pressure is nearly linear with temperature. The autoclaves were machined from purchased alloy billets. This work was done at the Thule Machine Company in Springfield, NJ. The volume of the autoclaves was about 20 cm<sup>3</sup>. This volume permitted the use of platinum liners (see section 3.2) to be constructed readily from thin wall platinum tubing. The Morey autoclaves are assembled and opened easily. They did require separate furnaces however, which were constructed at Airtron. Our design of autoclave duplicated that used at AT&T Bell Laboratory by R. Laudise. In this manner any runs and their conditions could be reproduced at both locations. This greatly facilitated some preliminary experiments and was most helpful in solubility determinations.

The workhorse autoclave for most KTA crystal growth in our program was the 1.5 inch system. To understand these larger systems in crystal growth, we first examine Figure 8 which is an idealized schematic of an operating autoclave. Nutrient of KTA

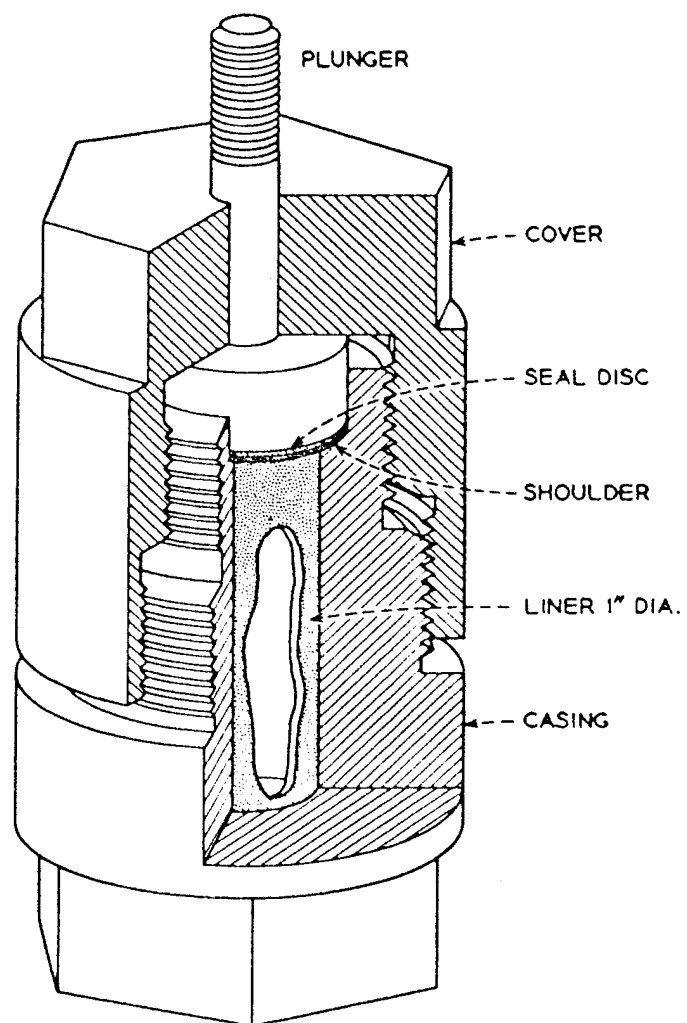


Figure 7      Morey type hydrothermal autoclave

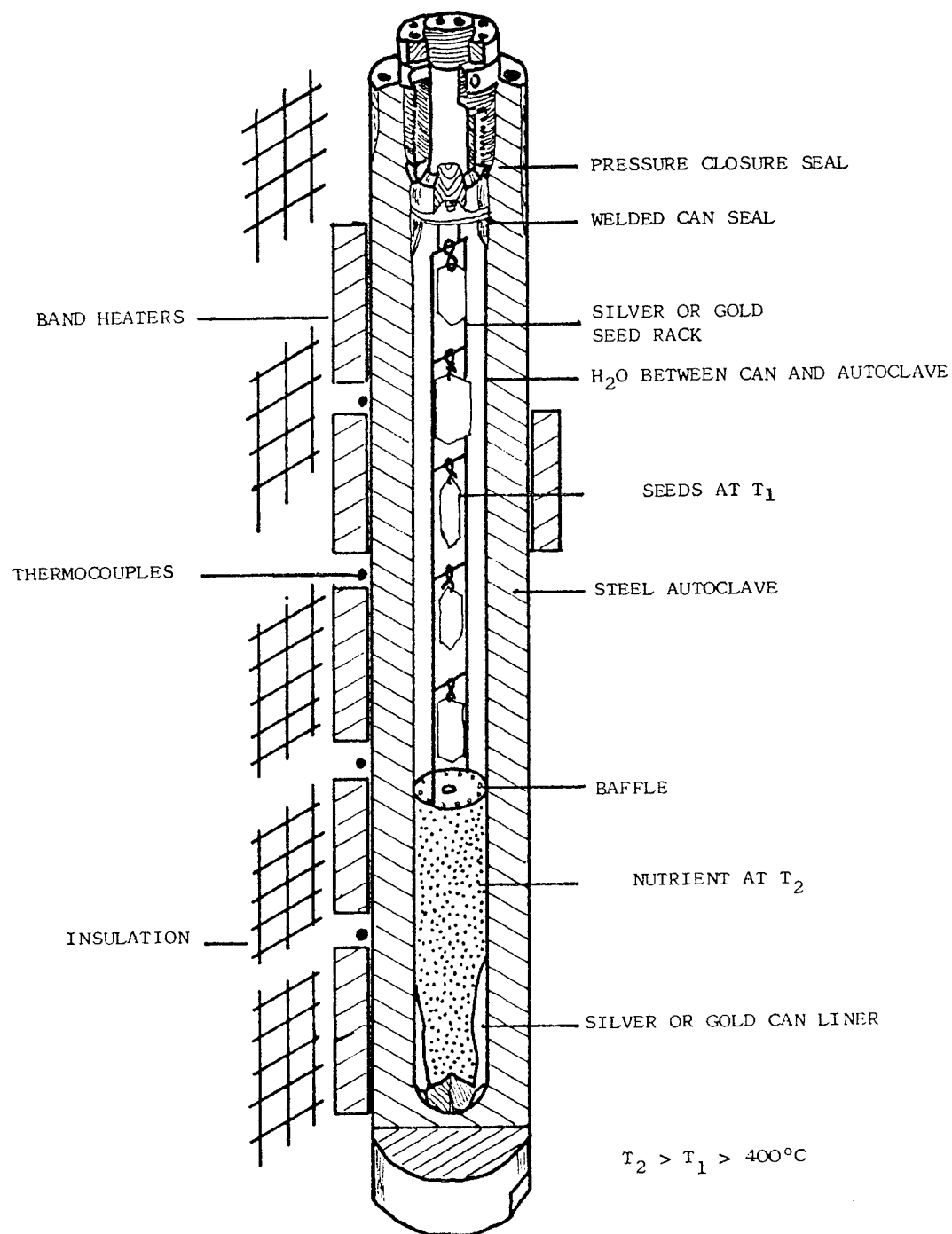


Figure 8 Hydrothermal system for KTA growth

is placed in the bottom and held at a temperature  $T_2$ . Seeds of KTA are affixed to a ladder and kept at a temperature  $T_1$ . A baffle separates the two thermal zones and serves to generate a thermal gradient with  $T_2 > T_1$  and  $\Delta T$  equal to about 10–40°C. Material of KTA at  $T_2$  is dissolved under the supercritical conditions and the fluid is transported to the cooler seed zone. It is here that the dissolved KTA deposits on the seed and grows in size.

The dimensions of these 1.5 inch cylindrical production autoclaves were as follows. The outside diameter was 3.0 inches and the total length was 21 inches. The inside growth cavity was 1.5 inch diameter and 18 inches long. Thus the working volume is in the range of 500 cm<sup>3</sup>. All of the autoclaves were constructed from the Rene' 41 alloys. The latter composition is about 50% Ni, 20% Cr, 10% Co, 10% Mo, 8–10% Fe. This alloy is highly resistant to corrosion, is good at the highest temperature and pressure, but is difficult to prepare and machine correctly. The autoclave was always fitted with a modified Bridgman seal which is most useful for hydrothermal growth. This seal is pictured in Figure 9. The initial seal that closes the vessel is made by tightening set screws to lock the plunger against a deformable gasket. The unsupported area closure makes its seal when the force of the heated solution acts upon the piston to move it up against the deformable gasket. In this sense, the seal is self-energized and becomes tighter at higher pressures. Of course the seal ring surfaces must be clean, smooth and reworked for each run. However, the seal heads are useful for hundreds of runs. Figure 10 illustrates the importance of nutrient size in the efficient operation of an autoclave. The small crystal nutrient in (b) permits unsaturated solution to freely circulate and dissolve the particles without "caking" as in (a). Thus mass transport to the seed is via particle-free saturated fluid.

### 3.2 Liners, Seed Holders and Baffles

Unfortunately all autoclaves are corroded to some degree by the chemical solutions they are intended to contain. This presents a problem because of cost, safety, and contamination of the contents. It is the normal case that corrosion increases with increasing temperature. Some mechanism must be employed to maintain the autoclave integrity while runs are progressing. At Airtron we have pioneered the use of noble metal liners of Ag, Au, or Pt coupled with the pressure balance method<sup>24</sup> to avoid rupture. In our experience gold was preferable for several reasons. Gold appears to be totally inert to all of our arsenate solutions at temperatures exceeding 600°C. Gold is extremely malleable and can be readily welded to give excellent closed vessels. Gold liners can be reused by reshaping the metal in an appropriate mold with pressure. There is no net loss of gold so the initial metal is never lost in production operation.

The gold liners we used in the 1.5 inch autoclaves were prepared from 99.95% fine gold seamless tubing. These were manufactured by Engelhard Precious Metals facility in Carteret, NJ. The tube dimensions were normally 1.45 inch outside diameter x 14.5 inch length with 0.040 inch wall. A 0.125 inch thick disk was welded

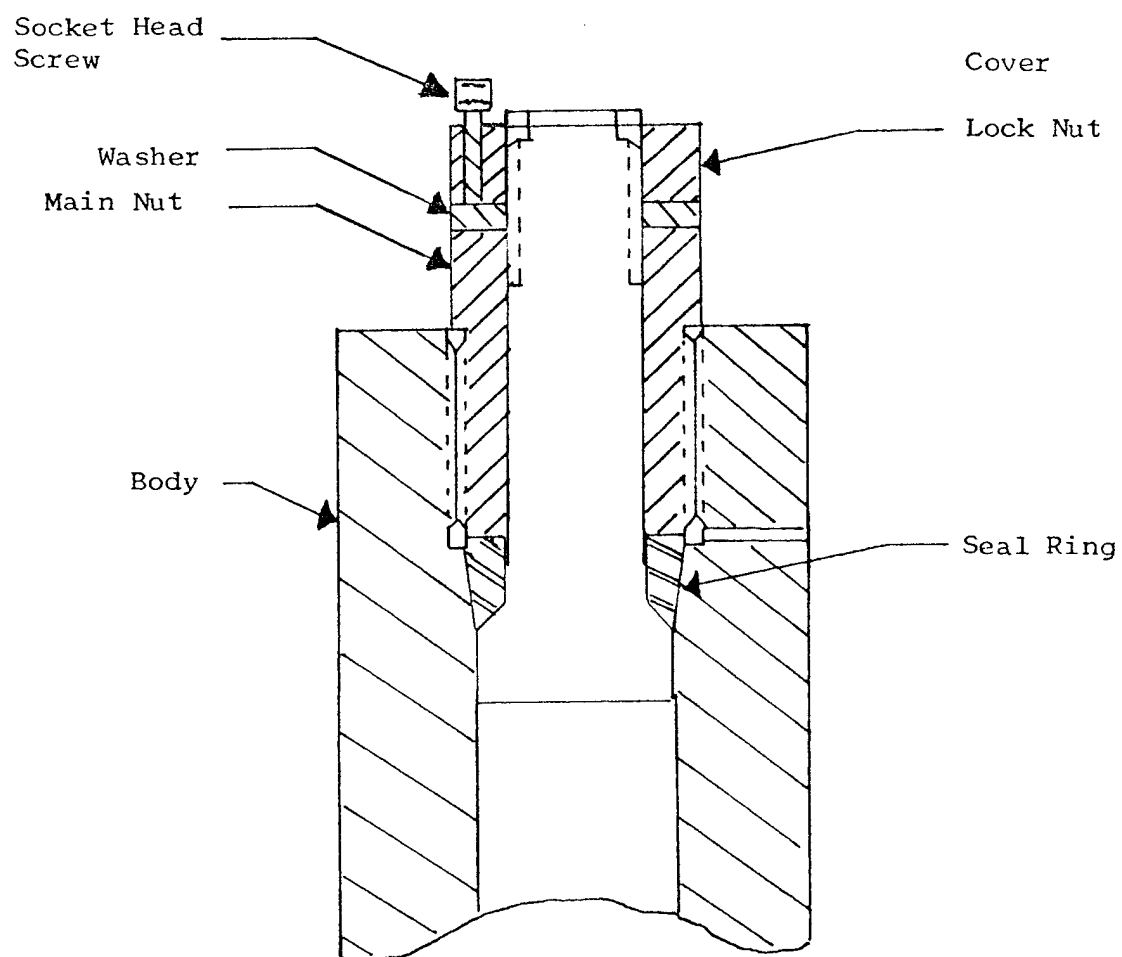


Figure 9      Sealing mechanism for autoclave

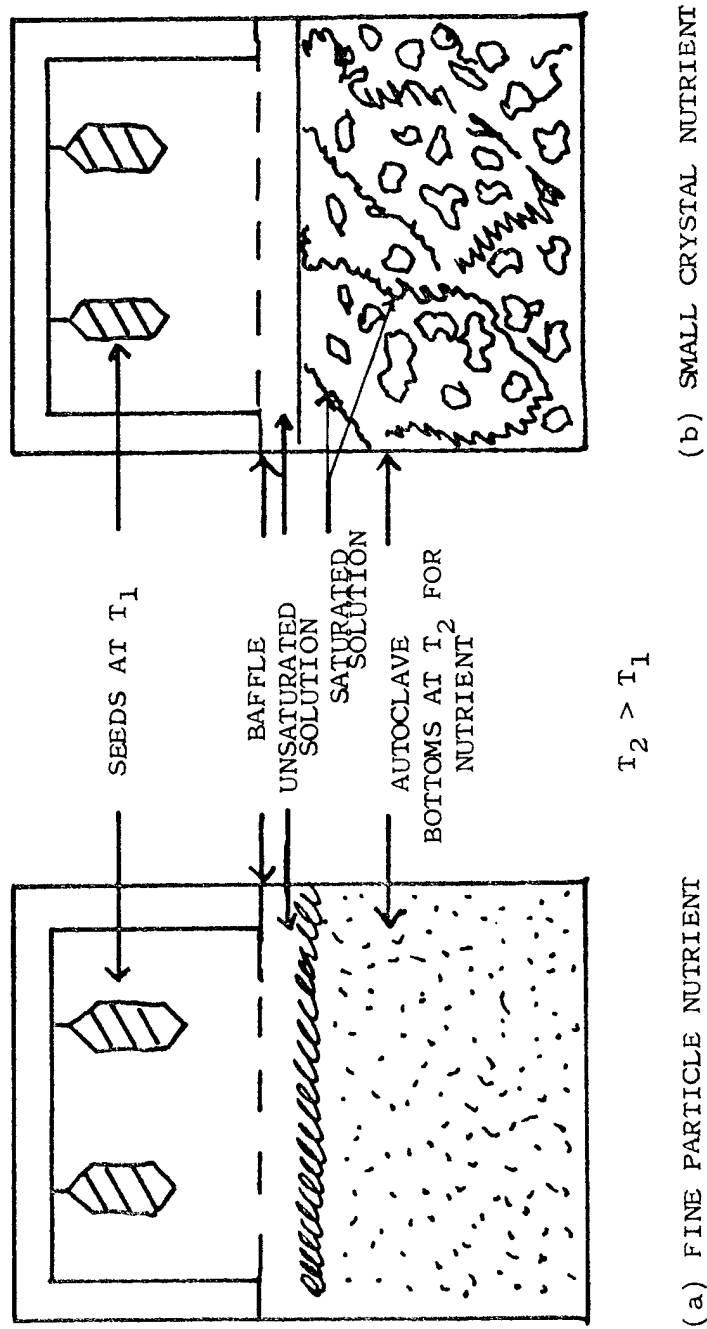


Figure 10 Importance of nutrient size in facilitating mass transport



to the bottom. The top disk had a 7.5 inch long ladder formed from .125 inch diameter gold wire. This ladder served to hold the 3 or 4 seeds located in the cold zone of the autoclave. At the bottom of the ladder a perforated disk was attached to serve as the baffle. The top disk also contained two spout holes for introducing liquids before sealing. After the appropriate solids of nutrient, seeds, and other chemicals were added, the liquids were introduced and then the spouts were sealed. A picture of the liner and parts is given in Figure 11(a), while 11(b) shows a ladder with seeds. The seeds are attached to the ladder by means of 0.010-0.020 inch diameter gold wire. Small holes are drilled in the crystals with a fine high speed drill. All of the metal welding is performed at Airtron with a Lincoln Electric welder as pictured in Figure 12.

A brief explanation of the perforated baffle is in order. The purpose of the baffle is to assist separation of the growth vessel into two nearly isothermal regions, the lower one at  $T_2$  and the upper one at  $T_1$ , with  $T_2 > T_1$ . The free open area of the baffle controls the uniform growth rate of the crystals. We have found that a suitable free area for growth of KTA lies around 25%. Values much smaller or larger tended to give non uniform growth in our 1.5 inch systems. We have also tried a single central hole in the baffle similar to that used in hydrothermal growth of quartz. However, the single hole was no improvement over the multiple 0.125 inch diameter holes we employed. At times during a run, one or more holes in the baffle may become clogged from SN (spontaneously nucleated) crystals. However, the effective area is changed only by a few % and growth occurs normally. At the end of a run, the top cap of the liner, with the attached seed ladder, is cut away to retrieve the grown crystals. The gold liner has some specific limitations in the use at 600°C and 25000 psi. It is essential that the pressure generated by the liner contents be approximately balanced by the pressure of the pure water located between the liner and autoclave. If this is not attained, the gold liner can rupture and possibly ruin the autoclave. Fortunately, the colligative properties of dilute solutions are close to and usually less than that of the pure water. Pressure balances have been obtained in our KTA growth by judicious use of the small autoclaves coupled with empirical data. Some recent attempts at pressure balance strategy have been reported for our systems<sup>25</sup>. For pure water, data have been compiled by Kennedy at high temperatures<sup>26</sup>. These data are invaluable for any hydrothermal work. Figure 13 shows a graph of his data for various fill %. For KTA, the proper adjustment of the % fill in the liner and outside the liner is required. These will be discussed further in Section 5.

### 3.3 Heaters Used

Originally, most hydrothermal growth systems were heated by a simple resistive element located at the bottom of the autoclave. Airtron, over the years, has perfected the use of cylindrical band heaters which can be strapped directly to the steel autoclave. In this arrangement, it is possible to attain finer control over both the nutrient and growth zones. Figure 14 shows a line drawing of a typical arrangement for our 1.5 inch diameter growth autoclave. The heaters are located to maintain a

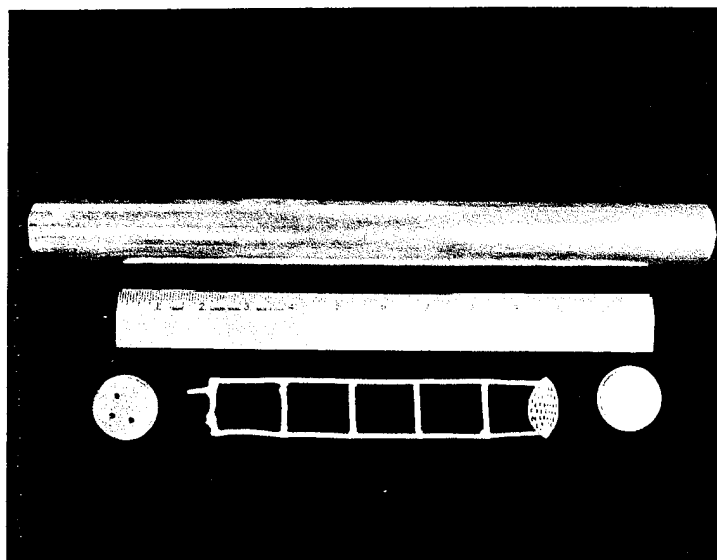


Figure 11 (a) Gold autoclave liner, end caps, and ladder

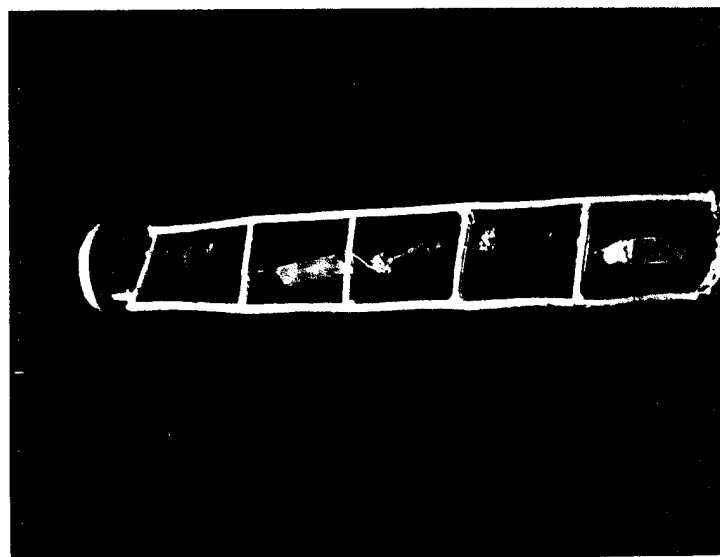


Figure 11 (b) Seed ladder with attached seeds

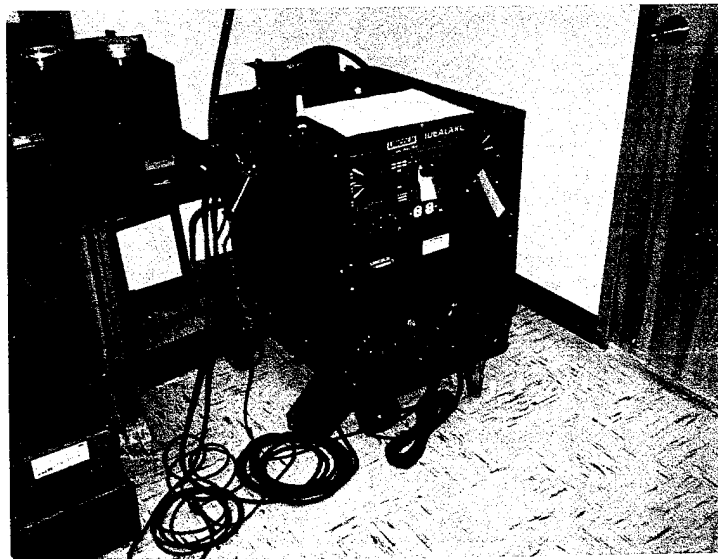


Figure 12 Lincoln Electric welder

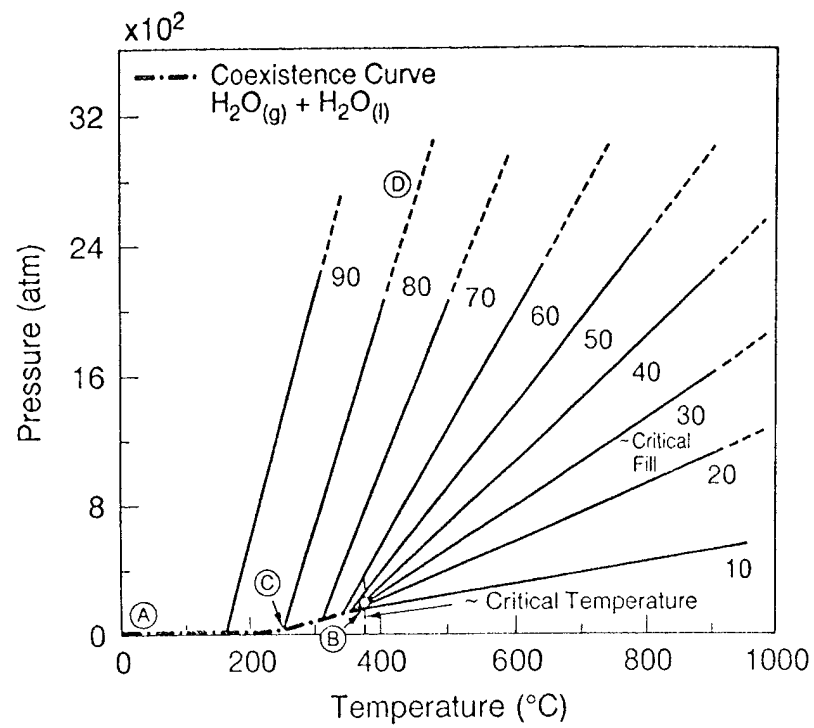


Figure 13 Pressure-Temperature-% fill for pure water after Kennedy<sup>26</sup>

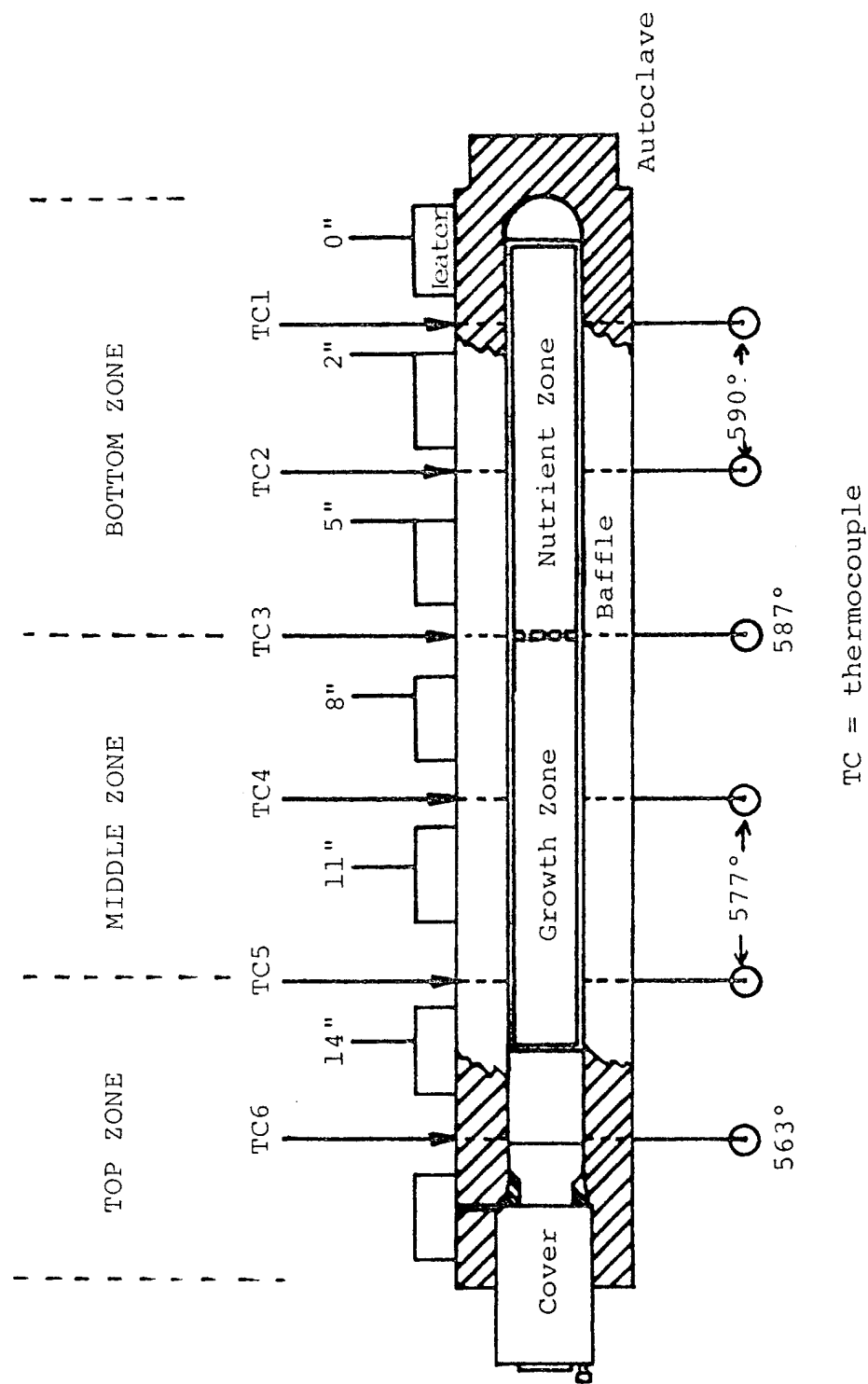


Figure 14 Airtron autoclave configuration

bottom nutrient zone at  $T_2 = 590^\circ\text{C}$  and a middle growth zone at  $T_1 = 577^\circ\text{C}$ . In this situation, a gradient of about  $\Delta T = 13^\circ\text{C}$  is maintained. Six thermocouples TC1 to TC6 are located between the heaters to measure temperatures at the surface of the autoclave. Notice that these temperatures do not depict exactly the thermal situation within the autoclave liner. However, they are representative, somewhat higher and functionally necessary to attain good growth reproducibility. It is necessary to maintain the liner top at the highest growth zone temperature in order to prevent excessive amounts of spontaneous nucleated (SN) crystals from forming.

The picture in Figure 15 shows a working autoclave with the strapped on heaters and thermocouples. There are seven heaters, each of about 500 watt capacity. Heaters were purchased from Industrial Heater Co.

Six thermocouples were placed between the heaters in the arrangement of Figure 14. For excellent temperature control, the heaters are divided into three thermal zones. The bottom zone contained three heaters, while the middle and top zone consisted of two heaters each. During operation the autoclave is insulated thoroughly by layers of Kaowool and particles of vermiculite. These are placed on the bottom, along the sides, and top in a reproducible manner. All of the insulation is surrounded by a double walled steel pipe measuring 20 inches O.D. x 17 inches I.D. x 5 feet long. This system is placed in a sub-surface cylindrical hole for safety purposes during operation. The system is covered by a steel safety cylinder at ground level. The latter easily contains any super critical water or solution if a leak ever occurs.

### 3.4 Pressure Regulation

In hydrothermal processes within a fixed volume, the pressure inside an autoclave is a function of temperature and degree of fill. For practical considerations, we must consider the autoclave at an isothermal temperature. Our liner fills (internal) were in the range of 70-90% while the pure water fills (external) were normally 5-20% less. Under these conditions, it can be seen from Figure 13 that the generated pressures are in the range of 2000 atm or 25000-30000 psi at  $550^\circ\text{--}600^\circ\text{C}$ .

Pressure was measured by Bourdon type gauges purchased from Pressure Products Industries of Warminster, PA. Autoclave Engineers of Erie, PA also sells a complete line of high pressure valves, tubes, fittings, gauges and other accessories to cover our working range of P-T. The Bourdon gauge utilizes a helical type element which is fastened at one end to the pressure connection and at the other to the pinion. Motion is transmitted from the pinion through an arm to a knife edge attached to the movement. The knife edge can be calibrated against a dead weight and adjusted to correct pressure or the length of the range blade changed. Pressure is read from the gauge at an accuracy of  $\pm 1\%$  of full scale.

The pressure gauge was connected to the autoclave via seals, tubing and a special three-way valve. Each gauge is also provided with electrical contacts to activate an

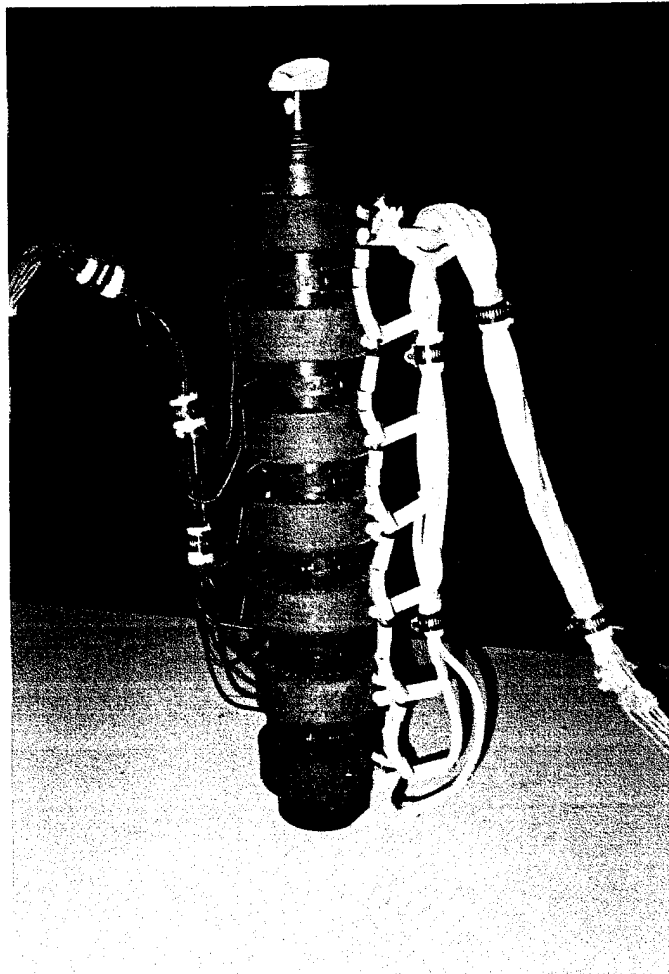


Figure 15

Picture of autoclave with strap--on heaters and thermocouples

alarm system in case pressure exceeds or falls below fixed limits which are preset. We have also used a pressure regulating air driven pump capable of high pressure. This pump can add or withdraw small amounts of water to regulate final operating pressure. Figure 16(a) shows a Morey type autoclave with pressure capillary tubing which connects to the Bourdon gauge. Figure 16(b) shows the thermal controls and blast proof box which surrounded the autoclave for safety. In Figure 17 the pressure gauge is the large dial located at the bottom of the rack which holds the electronic controls. All connections for the production facility are located in below ground tubes for safety reasons.

The 1.5 inch diameter autoclaves of Rene' 41 material were designed for maximum operating pressures of 30000 psi at 600°C. During their use we attempted to maintain run conditions well below these values. It is a fact of solubility, that with increasing pressure, the solubility of KTA also increases. Thus if too low a pressure is used, the solubility drops and hence the growth rate. It is advantageous to run the autoclaves under the highest temperature, pressure, and gradient which are consistent with safety.

### 3.5 Temperature Controls

As shown in Section 3.3, Airtron utilized the basic seven band heaters, three zone temperature control, and six measuring thermocouples on each autoclave. Our latest production system is computer controlled for a vast array of autoclaves, some of which are shown in Figure 17. The autoclaves are located below ground with the controlling elements on racks behind each unit. A central computer control room is located remotely and is illustrated in Figure 18. Each of the three thermal zones, bottom, middle, and top, is regulated by a three-mode controller. The controllers are combined in a master-slave configuration, where the middle and top zones maintain preset temperature differences relative to the temperature set on the bottom zone.

Each controller has an adjustable temperature set point, a relative percentage power output for the respective heater, deviation indicator, proportional band, rate, and reset functions. Trimming resistors are added for fine power control. The computer control gives reproducible heating rates, fine growth gradients, and excellent stability. Daily temperature readings are extracted from the thermocouples. These are readily converted to  $\Delta T$  values along the various positions of the autoclave. The most important data are bottom T, top T, and gradients of temperature. These functionally control the growth rate of the KTA crystals. The rate is directly of interest to us since it determines the length of the run, the quality of the crystal, and overall cost of the final material.

The growth rate of a crystal in solution is proportional to the amount of supersaturation (change in concentration), transfer rate of solution, and the area of the growing face. The supersaturation is determined by the temperature gradient between the nutrient and growth zones. This  $\Delta T$  is controlled partially by the

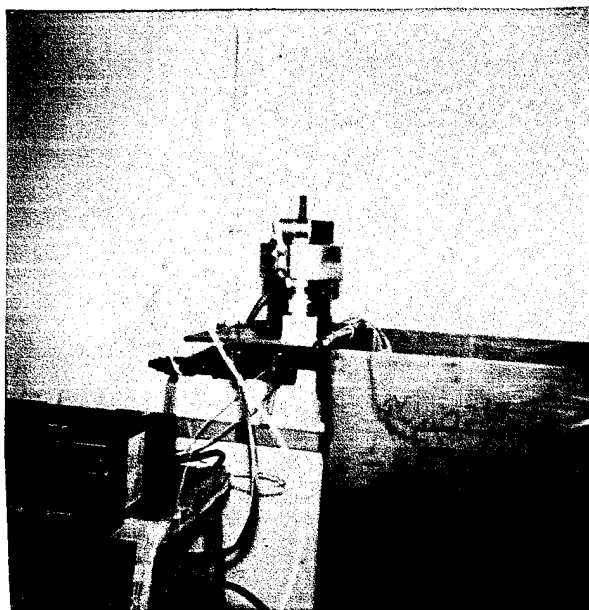


Figure 16 (a) Morey autoclave with pressure capillary

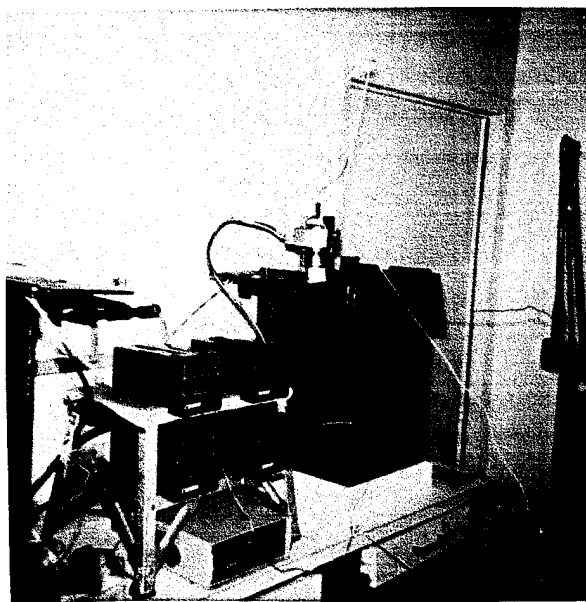


Figure 16 (b) Thermal controls and safety box





Figure 17      Production autoclave systems; KTA units are fitted with safety exhaust in lower right

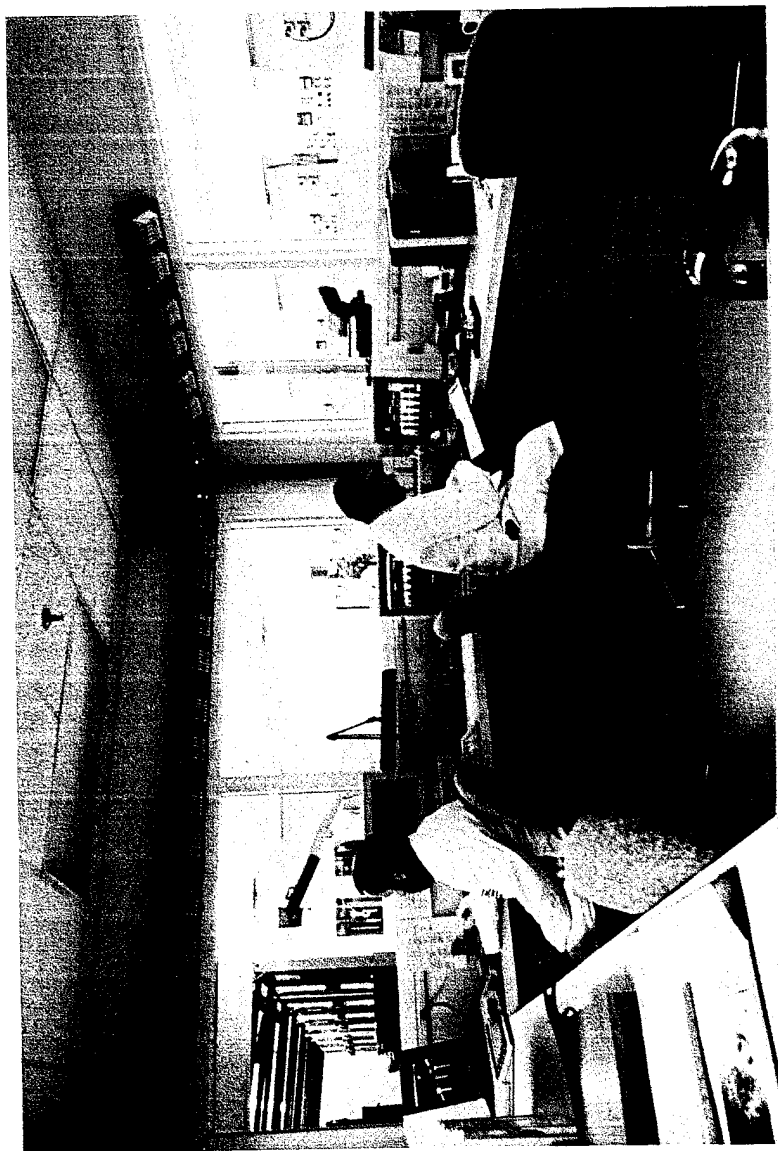


Figure 18      Computer control room for autoclave operation

physical location, state, and open area of the baffle. The baffle also controls the mass transfer rate which is primarily determined by density differences between the hot saturated solution and the cooler spent solution at the seed. The density difference is again a function of the temperature gradient. The study of the growth rate is complex and involves parameters which are difficult to control. In our KTA growth, it is apparent that increased growth rates generated by ever increasing  $\Delta T$ s tended to decrease overall visible internal crystal quality.

With reference to Figure 14, the thermal gradient is taken to be the difference between temperatures measured at positions TC1 and TC4. The overall gradient, defined by the  $\Delta T$  between positions TC1 and TC6, is also important since it controls somewhat the total mass transfer rate. The latter includes growth on the seeds plus any SN material which is polycrystalline. As a general rule, it was very difficult to raise  $\Delta T$  (1-4) without increasing  $\Delta T$  (1-6). The SN material collects naturally at the coolest part of the autoclave which is always the top end. It is desirable to mitigate the formation of SN while trying to increase the actual growth rate on the seeds. This procedure is a bit empirical but achieves results. More data on KTA growth rates will be given in Section 5.0.

### 3.6 Run Procedures

Reproducible procedures were developed for the running of each autoclave whether large or small. The 1.5 inch diameter production systems were in constant operation after the first year of the program. Results are dependent on trained technicians, accuracy of measurements, and constant attention to numerous details. We give here a general description of our techniques for the 1.5 inch system. Each autoclave is prepared by rigorous cleaning of the interior and final inspection. Particular attention is given to the pressure sealing surfaces, tube seals for pressure, and all fittings. The gold liner is also cleaned to remove dirt, previous chemicals, or other foreign matter which may cause crystal nucleation. A reused liner may have to be reshaped to a neat cylinder. For the autoclave itself, special jigs and tools are required for sealing and removing all pressure fittings. All additions of chemicals to liner and autoclave are performed in a clean room to avoid contamination. For the arsenic containing chemicals, rigid safety in handling is necessary.

The liner is first half-filled with KTA nutrient and part of the mineralizer solution. More solution is added after the baffle-ladder assembly with seeds is lowered into the liner. The liner is then welded shut except for an open fill spout at the top. During welding of the top cap, the liner is surrounded by cold water. Any remaining chemical is dissolved in a measured quantity of water and the resulting solution is added through the spout. The spout is then welded shut. The liner's volume is measured, the liner is checked for leaks and then inserted into the autoclave. Pure water is added to the volume between liner and autoclave. The autoclave is then sealed, and lowered into the shield. The system is brought to operating temperature and desired temperature gradients are established by adjusting controller setpoints.

Pressure is adjusted by pressurizing or bleeding the system with pure water. At the end of a run, the system is returned to standard T-P by shutting off power. The autoclave is opened and the liner removed. The liner is then cut open and the crystals are removed, washed, and measured to obtain growth rate. The autoclave and gold liner are reworked and prepared for the next run. A careful log is kept for each autoclave. This includes hours of operation which have accumulated and dimensional measurements.

It should be stressed that all of the chemicals used in our runs are weighed. This enables concentrations, solubilities, and other chemistry to be described on a quantitative basis. Furthermore, the correct volumes of the autoclave, liner, and chemicals must be known to ascertain the fill percentages, calculate pressures, and reproduce a run. Some important measured data are obtained and volumes are calculated from these data on various parts of the liner, autoclave, cover, cap and space between liner and autoclave. For example, we measured the volume of the autoclave, external and internal volumes of the liner, volume of the cover cap, volume of solution in the liner, and volumes of pure water between liner and autoclave. These data are converted to % fills which are required for pressure balance under operating conditions. It should be noted that each autoclave and liner is slightly different from the others. Furthermore, additional dimensional changes occur from run to run. Our quantitative data assist in preparing each run to be reproducible in its starting conditions.

#### 4.0 Solubility Studies

In order to grow crystals by the hydrothermal method, some measure of the KTA solubility in various solutions must be obtained as a function of temperature and pressure. For normal solution behavior, solubility increases with increasing temperature and pressure. Solubility is most sensitive to temperature even though there is pressure dependence to a lesser degree. The larger slope of the solubility-temperature curve enables crystals to be grown at relatively low thermal gradients in the range of 5-50°C. The quantitative value of the solubility at operating conditions need not be high; typically, values of 1-5 weight % are satisfactory. However, it is advantageous to have higher solubility because lower temperatures and pressures reduce the autoclave material cost, growth rates are relatively high, and only small gradients are required. It is not possible to predict or calculate the solubility curve. Empirical methods are required throughout and some intuition is required on choice of solvents.

#### 4.1 Run Description

Solubilities of KTA in various mineralizers were measured by the weight loss method using single crystals grown from the  $\text{WO}_3$  flux. Small platinum capsules were contained in Tuttle type autoclaves where pressure was provided by means of water pumped by a compressed air driven intensifier. The technique follows that of Laudise and coworkers<sup>27</sup> for many materials. Mineralizer solutions are prepared and added to the capsule by means of a micro syringe. Weighed KTA crystals are held by platinum wire from the top of the capsule. The capsules are filled to a fixed fraction of its free volume. Our capsules were typically 3-4 cm long x 0.4 cm diameter and had internal volumes of 0.2-0.3 cm<sup>3</sup>. Internal fill and external fill were chosen to approximately balance the respective generated pressures in order to prevent crushing or rupturing the capsule. The capsules were crimped, then welded, and placed in the autoclave. Figure 19 gives an example of one sealed capsule. Once the capsules were in the autoclave, they were heated to the desired temperature with a furnace which slides over the autoclave. The entire autoclave in this case should have no major thermal gradients and the capsule can be treated as an isothermal system at fixed pressure. The run is equilibrated at a temperature T for several days. Following the run, the autoclave is quenched to room temperature, opened, and the capsule removed. The capsule is cut open and the weight loss of the KTA is calibrated.

Figure 20 gives a rough solubility curve determined for KTA crystals under the conditions of a pressure equal to 30000 psi, up to temperatures of 600°C, and using a mineralizer solution of  $\text{KOH-KH}_2\text{AsO}_4$ . This curve was specifically for 12M  $\text{KH}_2\text{AsO}_4$  at a K/As mole ratio of about 1.0. Similar curves are obtained at different K/As ratios. If the pressure is now reduced from 30000 psi, the solubility decreases slightly but the data spread has increasing error which obscures good results. In this

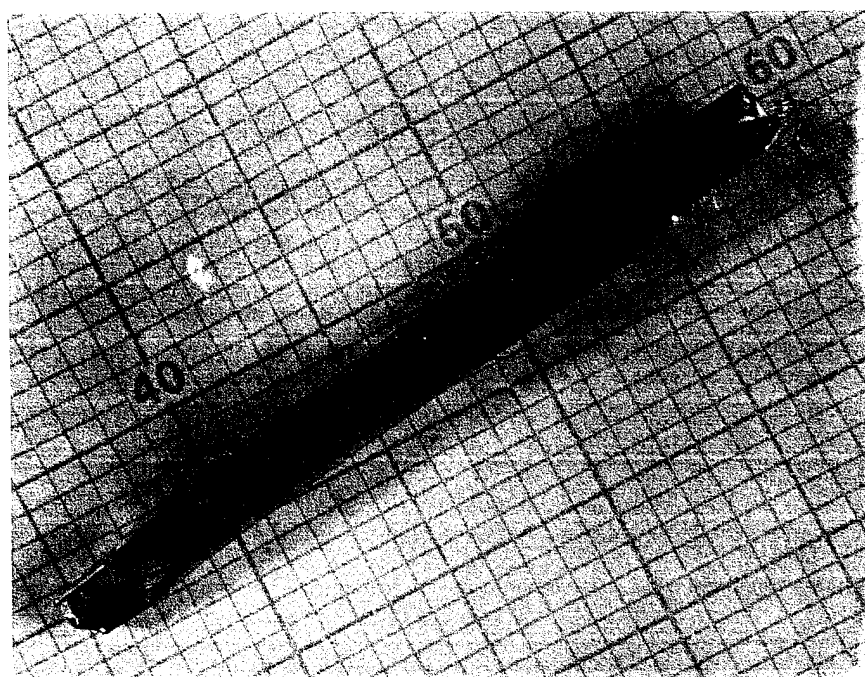


Figure 19

Small platinum capsules useful for solubility and phase studies

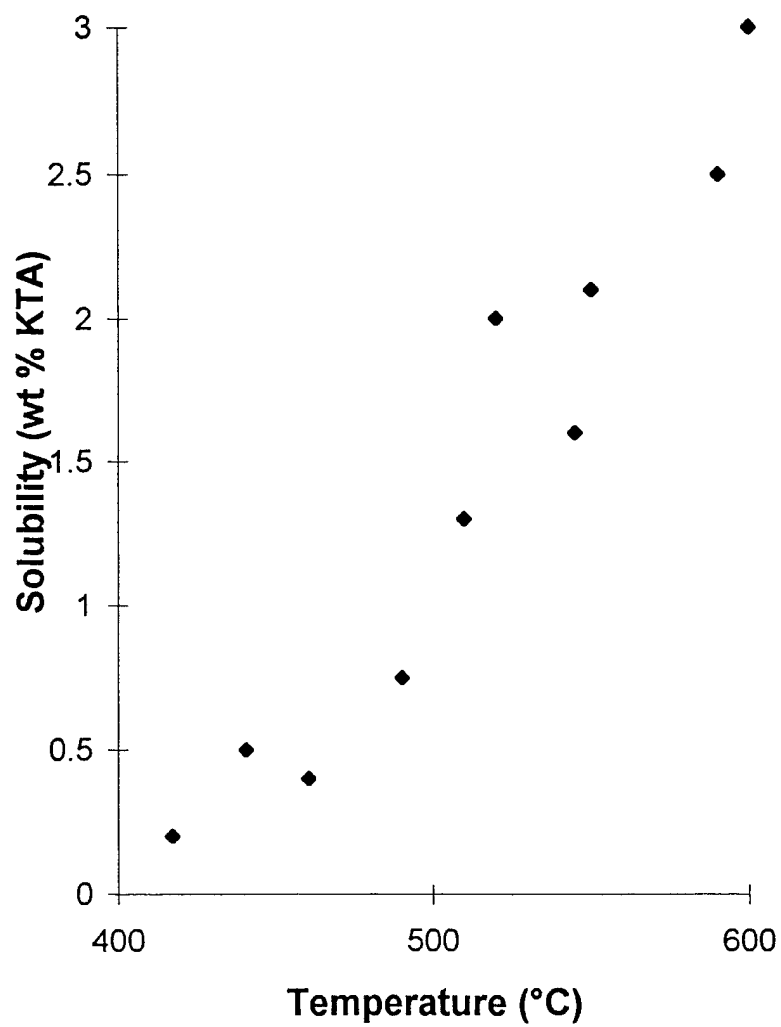


Figure 20

Solubility curve for KTA at 30,000psi in KOH-KH<sub>2</sub>AsO<sub>4</sub>

case the pressure dependence is almost negligible. Notice that the solubility of KTA at the upper temperature range is about 2.5-3.0 weight %. This is less than the 4-5% determined for KTP in some  $K_2HPO_4$  solvents<sup>28</sup>.

In Table III we present some data on the solubility of KTA in mixtures of KOH- $KH_2AsO_4$ . The data were collected near the upper operating limits of our production autoclaves, 30000 psi and 600°C. The results were recorded in matrix form where various solubilities are plotted as a function of K/As molar ratio at specific molar concentrations. The purpose of this group of experiments was to locate the optimum solubility for scale-up to 1.5 inch systems. The solubility values are given in weight % and not all combinations were attempted. It is normally necessary only to determine favorable conditions or trends among the data. For example, the highest values of solubility are located at 4M  $KH_2AsO_4$  with K/As = 1.0 and at 12M  $KH_2AsO_4$  with K/As = 1.3. Indeed, both of these compositions will grow KTA when used in large autoclaves. It is important that KTA is the only solid phase crystallizing in the system. Compositions near the lower right corner of the matrix yielded  $K_2Ti_6O_{13}$  and  $As_2O_5$  in addition to KTA. Therefore we are probably going out of the stable phase region for KTA.

It should be realized that under the circumstances of the solubility measurements, there can be a fair amount of error in the absolute results. An example of this is given in Table IV where solubility results are reported on similar systems from experiments conducted at three separate laboratories: DuPont, Bell Labs, and Airtron. The solubility trends are similar at all laboratories. Good agreement between Airtron and Bell Labs probably occurred because the autoclaves and techniques were nearly identical. The DuPont data appeared consistently lower since their autoclaves were of different design and equilibration times were of shorter cycles. Subsequent large runs at Airtron have proved that good KTA growth occurs at 9-12M  $KH_2AsO_4$  with K/As ratios around 1.1-1.4. Furthermore, only KTA crystallizes. Basically, the data have been verified at four separate laboratories so a firm basis was available for large autoclaves.

#### 4.2 Phase Results

Phase studies are performed in a manner similar to those of solubility. The basic small autoclave of Tuttle design is employed with the sealed platinum capsules. Weighed amounts of chemicals are introduced into the capsules, they are welded shut, and then put into the autoclave at specific temperatures and pressures. After a period of equilibration of 4-6 days, the autoclaves are quenched to normal T-P, the capsules are removed and the contents analyzed. In order to perform many experiments simultaneously and obtain data quickly, the Tempress equipment is a necessity.



Table III

Solubility of KTA  
 In KOH -  $\text{KH}_2\text{AsO}_4$   
 30,000 psi @ 600°C  
 Weight %

K / As Molar Ratio	1.0	2.3		1.7
	1.1			
	1.2		1.6	1.6
	1.3			2.3
	1.4	1.7	2.1	1.5
	1.5			0.6
	1.6			$\text{K}_2\text{Ti}_6\text{O}_{13}$ & $\text{As}_2\text{O}_5$
		4	8	12
		Molar $\text{KH}_2\text{AsO}_4$		

Table IV

Solubility of KTA  
In KOH -  $\text{KH}_2\text{AsO}_4$   
30,000 psi @ 600°C  
Weight %

		DuPont			
K / As	1.0	0	0.1		0.1
Molar	1.2	0	0.1		0.2
Ratio	1.4	0	0.2		0.3

		Bell Labs			
	1.0				1.7
	1.2			0.3 0.3	0.3
	1.4			0.2	0.8 0.6 1.0

		Airtron			
	1.0				
	1.2		1.6		1.6
	1.4		2.1		1.4 0.4 0.2
		4	8	10	12

Molar  $\text{KH}_2\text{AsO}_4$

Several instrumental tools were invaluable for the identification of any compounds in our phase studies. We used optical microscopy, electron microscopy, the electron microprobe, and X-ray diffraction extensively. The results were always checked at other independent laboratories. Some examples of the results will be given but for the most part they are straightforward. Most compounds crystallize in a unique morphology and can be identified by observation. For KTA, a specific orthorhombic form is always present as in Figure 21(a). At normal T-P, KTA is insoluble in water while all other arsenates are soluble. Figure 21(b) shows  $\text{TiO}_2$  crystallizing as fine needles of  $50\mu\text{m}$  size. The microprobe can determine elemental constituents of tiny crystallites, elemental ratios, and identification of compounds. In Figure 22(a) we show an elemental probe of polycrystalline KTA from a  $\text{WO}_3$  melt and used in a gold liner. Traces of W and Au evident. In Figure 22(b) we show a portion of KTA crystal grown in a gold liner. In Figure 22(c) a probe analysis from an  $8\mu\text{m}$  particle of KTA is shown. This material was from a quenched nutrient prepared in platinum crucibles. Figure 23 shows an X-ray diffractometer scan of ground microcrystalline KTA obtained by pulverizing KTA crystals grown from a flux. Easy identification of any compound can be done by X-rays. In Table V we list the X-ray single crystal unit cell lattice constants for a number of isomorphs. All of these compounds have the same orthorhombic unit cell with similar internal coordinates. The increased size of ions through the series K, Rb, Cs and P, As determine a, b, and c.

Phase results are required to prepare diagrams such as that in Figures 2 and 3. These are descriptive plots of data which correlate many individual experiments. If a diagram is available, it saves much needed effort and does not have to be repeated. At Airtron we started our program with KTA phase data which was provided by DuPont. Of course, this was supplemented by an extensive investigation of our own on various mineralizers, changing conditions of pressure and temperature, solubilities, and growth rates. All of this was achieved in the first year to prepare the way for a planned increase of scale in our 1.5 inch production systems. The remaining problem of larger seeds was solved by two methods: (1) availability of seeds from large flux runs, and (2) Repeated growth by hydrothermal means to increase size.

#### 4.3 Growth Rates

The kinetics of crystal growth is governed partially by the actual growth conditions, such as temperature, pressure, and amount of supersaturation; also, the mass transfer of solute and the respective areas of growing faces play a part. We refer first to several morphology diagrams as pictured in Figure 24 for KTA. It should be recalled that the equilibrium growth faces in any crystal are the slowest growing ones; they are determined by structural data and relative atomic density in most cases. Figure 24(a) shows how an idealized KTA crystal looks when crystallized from a flux, in this case  $\text{WO}_3$ . Prominent planes are marked, e.g. (100), while the axes are A, B, C. In Figure 24(b) we illustrate a crystal grown from an  $\text{KH}_2\text{AsO}_4$  solution under hydrothermal

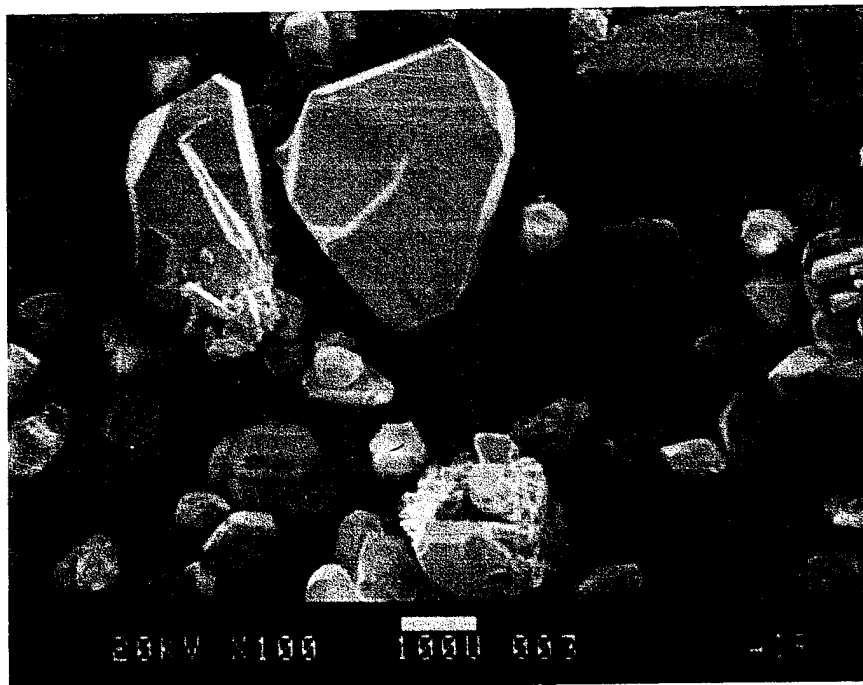


Figure 21 (a) Electron micrograph of polycrystalline KTA, 10-100 $\mu$ m particle size

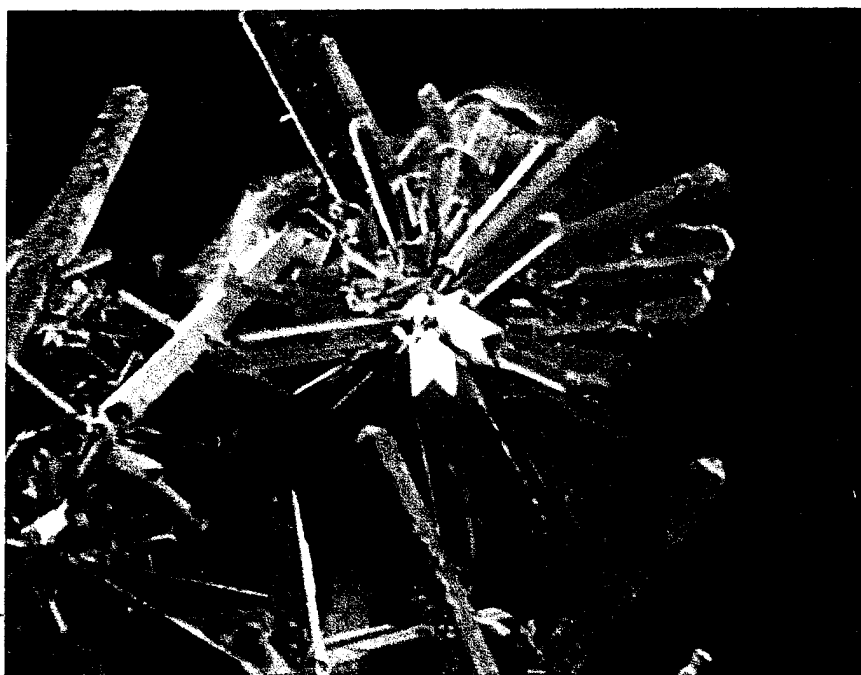
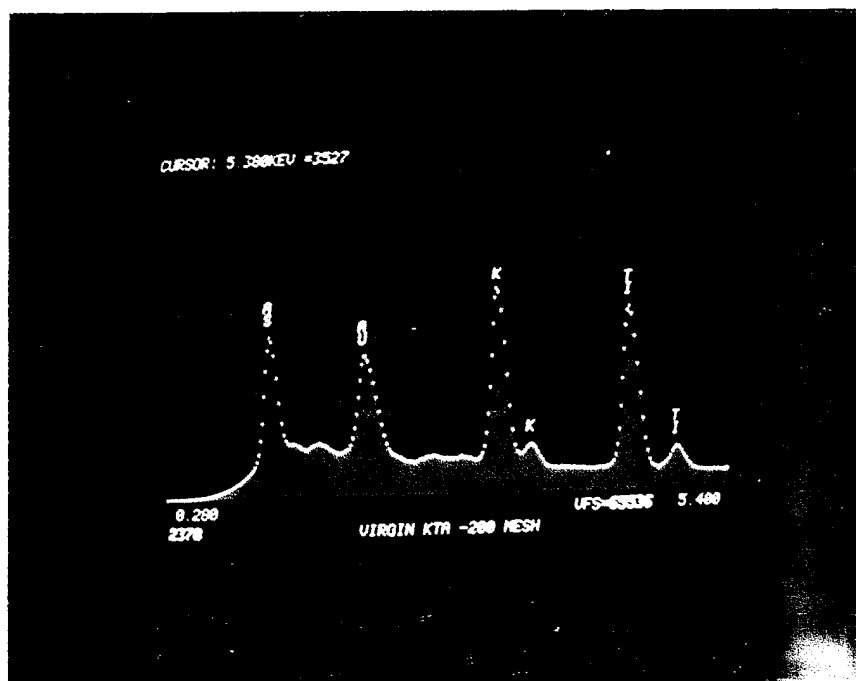
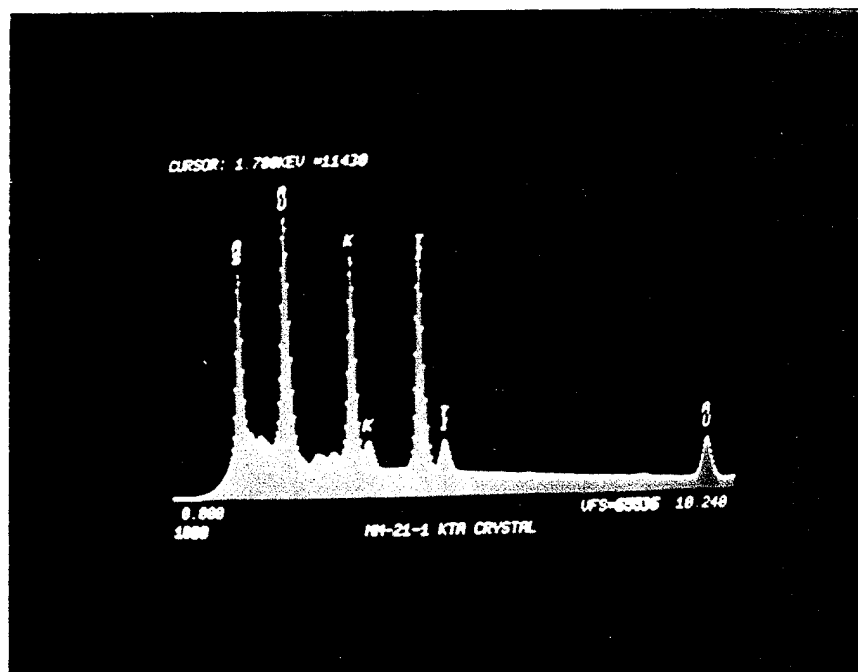


Figure 21 (b) Crystallized needles of rutile TiO<sub>2</sub>, 50 $\mu$ m



↑ ↑

Figure 22 (a) Microprobe of KTA from  $\text{WO}_3$  melt



↑  
W

Figure 22 (b) Microprobe of KTA crystal grown in gold liner

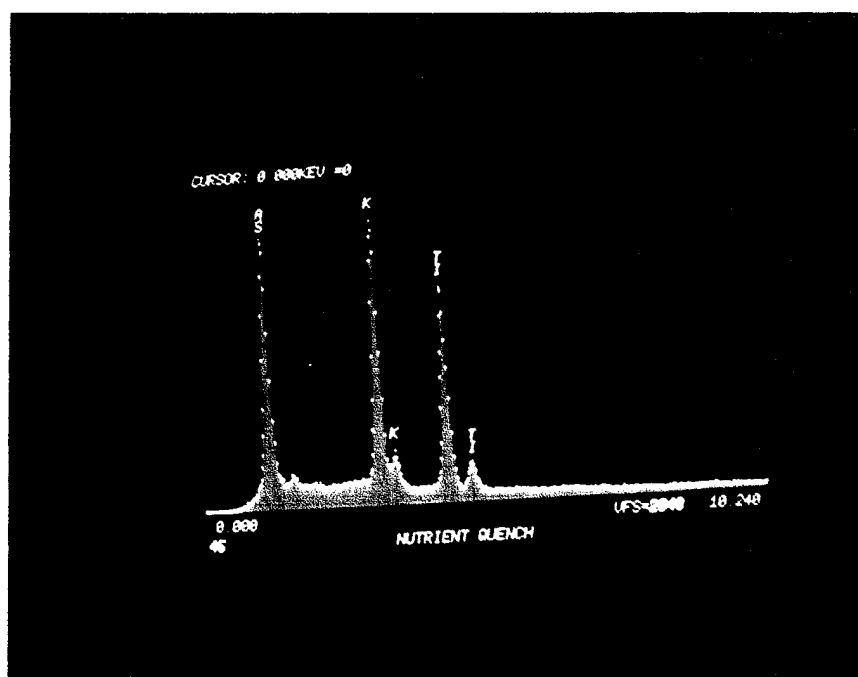


Figure 22 (c) Microprobe of 8 $\mu$ m KTA from quenched nutrient

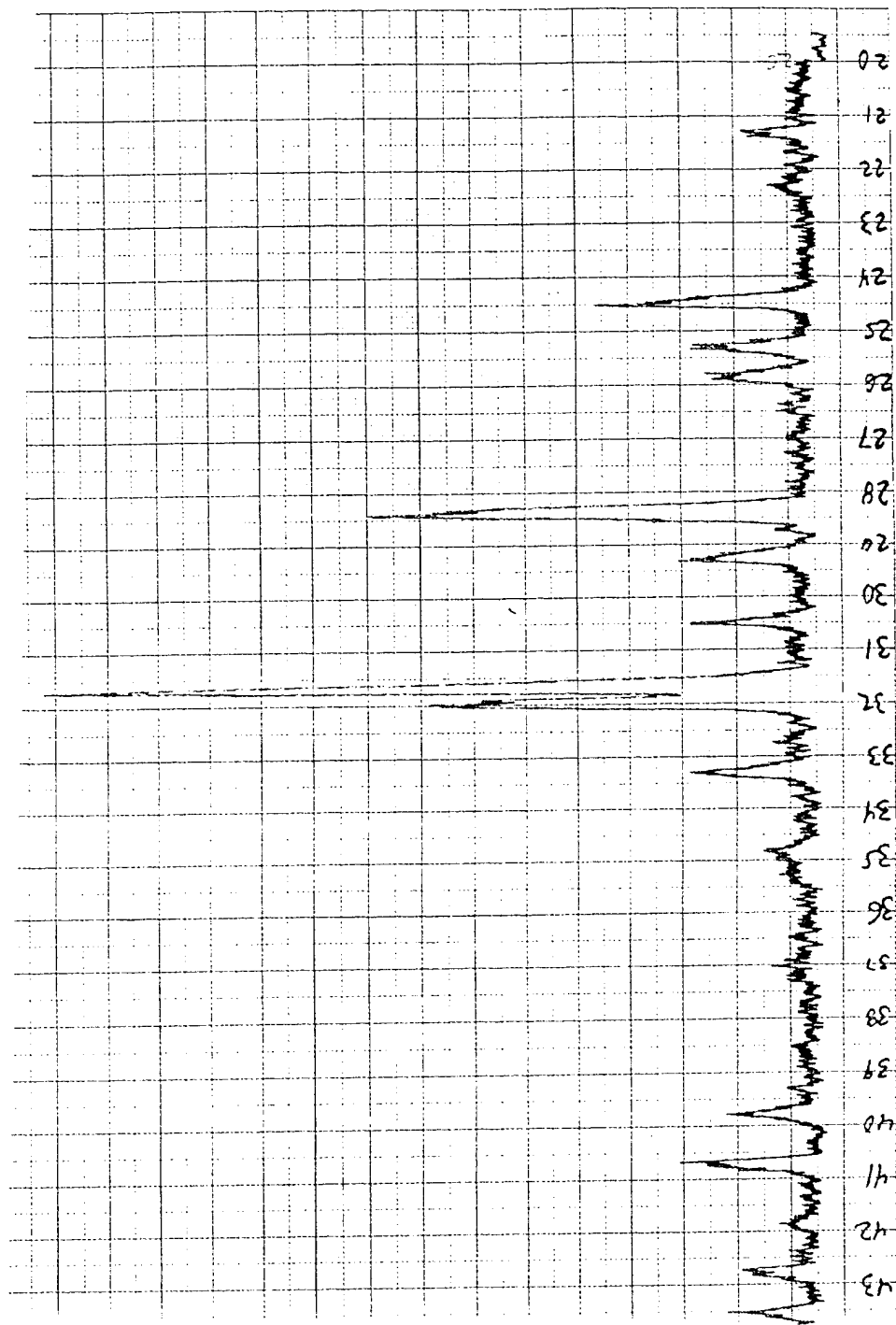


Figure 23 X-ray diffractometer scan of KTA micro-crystallites from flux

Table V

## Lattice constants for several KTP isomorphs

Crystal		Lattice Constants (Angstrom)			Cell Volume
		a	b	c	( $\text{\AA}^3$ )
KTiOPO <sub>4</sub>	KTP	12.822	6.4054	10.589	869.67
RbTiOPO <sub>4</sub>	RTP	12.964	6.4985	10.563	889.89
TiTiOPO <sub>4</sub>	TTP	12.983	6.490	10.578	891.30
KTiOAsO <sub>4</sub>	KTA	13.125	6.5716	10.786	930.31
RbTiOAsO <sub>4</sub>	RTA	13.258	6.6781	10.766	953.20
CsTiOAsO <sub>4</sub>	CTA	13.486	6.8616	10.688	989.02
TiTiOAsO <sub>4</sub>	TTA	13.208	6.6865	10.724	947.09
KGeOPO <sub>4</sub>	KGP	12.602	6.302	10.006	794.65
KSnOPO <sub>4</sub>	KSP	13.146	6.5280	10.727	920.56



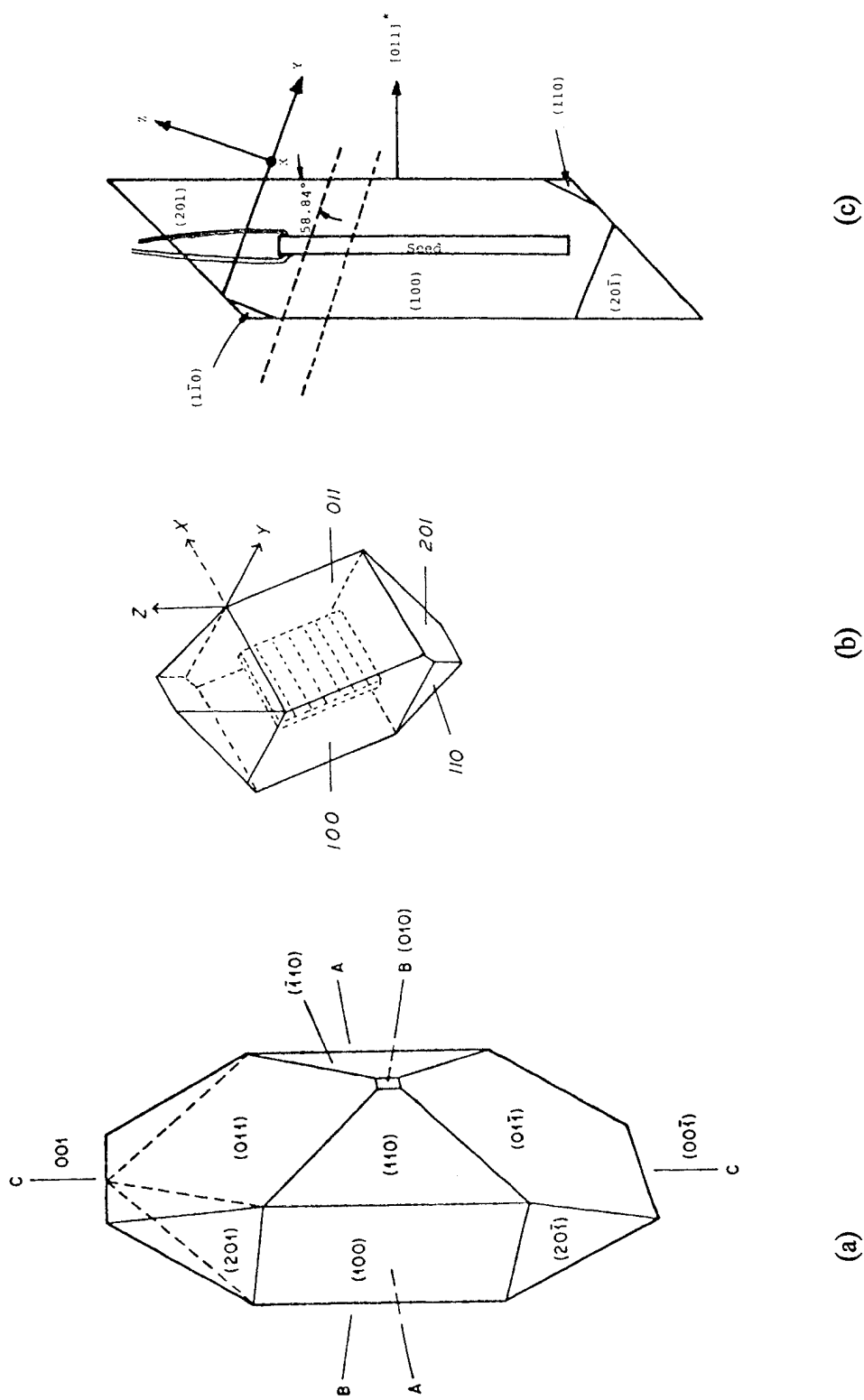


Figure 24 KTA crystal morphologies (a) from flux, (b) from hydrothermal growth on  $(011)$  seed  
(c) cross-section of hydrothermal crystal with view parallel to  $(011)$  seed plane

conditions. The (011) seed is outlined by the dotted lines. Again, some prominent planes are indicated with crystal axes X, Y, Z. Figure 24(c) is a similar hydrothermal crystal with the view along the major (011) seed faces. The diagram shows an approximate cutting angle for slabs which were then used for frequency doubling.

Growth rates are usually calculated from data taken early in our large hydrothermal runs. Seed crystals are cut from flux grown KTA in a known planar orientation. These different seed orientations are all placed in the same autoclave and exposed to the same growth conditions. Each crystal has been weighed and its thickness measured before the run. Growth is then performed for a 5-10 day period. After this time, the autoclave is cooled, the liner is opened, and crystals are weighed and measured again. It is convenient to express growth rates in terms of mm/side/day or week. Notice that growth occurs on both sides of a seed at slightly different rates because the crystal is acentric. We have tried mainly the (100), (201), (110), and (011) orientations of KTA as given in Figure 24(b). The relative growth rates are  $(100) > (201) > (011) > (110)$ . However, for practical purposes, we desire a nearly equidimensional crystal for processing. Some orientations like (100) lead to severe "capping" and yield a flat crystal even though the rate is good. For all of the subsequent large runs, we have found the (011) orientation to be most useful. Absolute growth rates of up to 1 mm/side/week could be sustained in our systems. These are slightly less than those for KTP growth under similar conditions.

#### 4.4 Pressure-Temperature Effects

For large autoclaves, successful runs must be conducted under near-pressure-balance conditions between the pure water (located between liner and autoclave) and the solution contained within the liner. Once a satisfactory mineralizer is confirmed, it is expedient to perform a few experiments on fill ratios. This may be done in the small Morey or large Bridgman seal autoclaves. Essentially we require P-T data for various fills. In our case, we used the 12M  $\text{KH}_2\text{AsO}_4$  solution at a K/As ratio of 1.4. Seeds were even put in the autoclave for run simulation.

Figure 25 shows a plot of the actual data where pressure is recorded as a function of temperature. Above the critical point for water at 375°C, it can be seen that these curves are linear and can be extrapolated. Each curve represents a different fill in %. Thus, 86-63 refers to the inner-outer fills respectively. The outer fill is pure water and is always less than the inner which is solution. Practical results are evaluated in terms of what happens in a run, particularly to a liner. On Table VI we summarize the main results which indicate that at inner-outer fills of 77.5-57%, we obtain the approximate balance for this mineralizer. We have also indicated the growth rates attained for three seeds of specific orientation. The next Section 5.0 describes an extensive series of large runs which yielded sizeable high quality crystals.

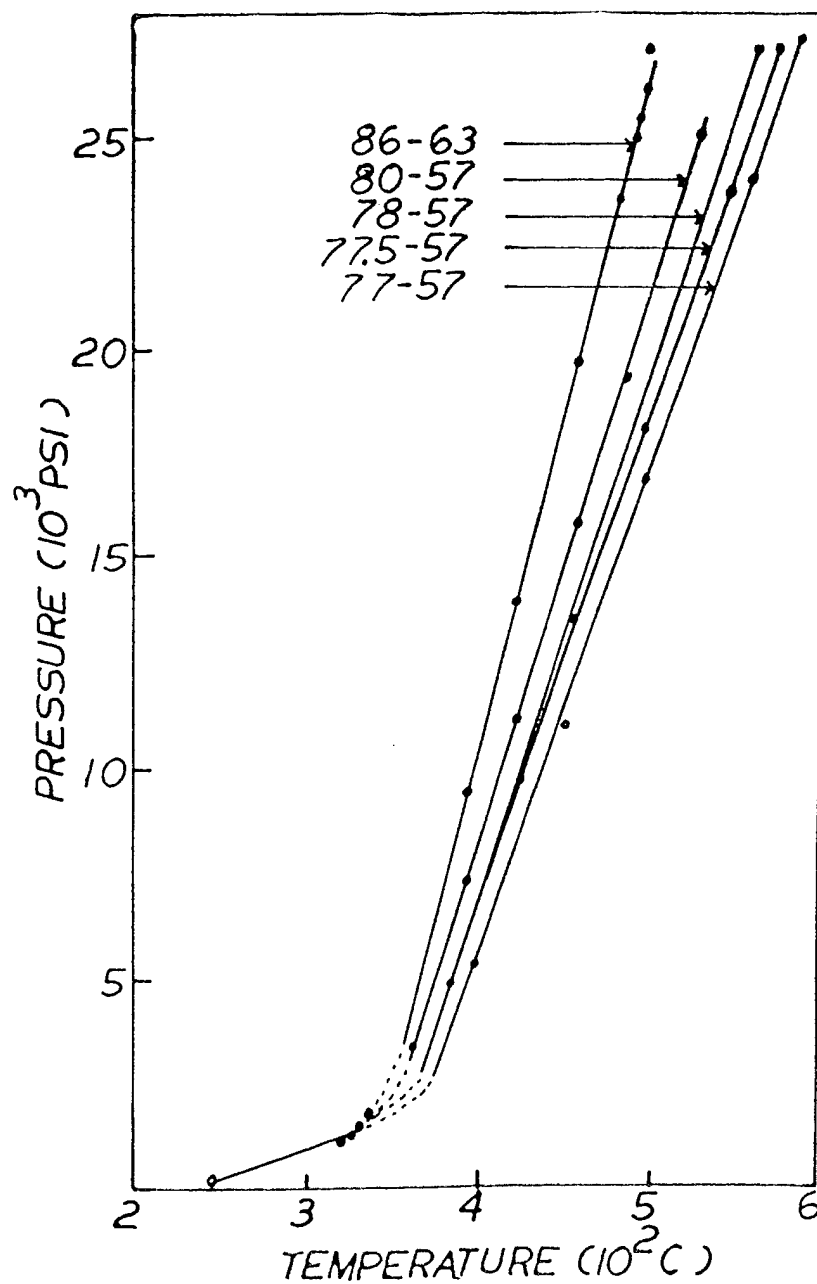


Figure 25

Pressure-temperature data for various fills: Inner-Outer %

Table VI

Pressure Balancing Results

12M  $\text{KH}_2\text{AsO}_4$  &  $\text{K} / \text{As} = 1.4$

<u>Inner fill, %</u>	<u>Outer fill, %</u>	<u>Remarks</u>
77.0	57	under pressure
77.5	57	pressure balanced
78.5	57	over pressure
80.0	57	over pressure
85.0	57	over pressure

Growth Rates:	(201) and (011) KTA	1.0 mm/side/week
	(011) KTP	0.75 mm/side/week

## 5.0 Growth Run Scale-Up

### 5.1 Run Description

Having determined the solution chemistry, a series of runs was done in 1.5 inch autoclaves under conditions similar to the production growth of KTP crystals. The following conditions were essentially constant for the series of nine KTA runs:

autoclave size	1.5" ID x 18" long
protective liner	sealed gold can
Molarity of $\text{KH}_2\text{AsO}_4$ solution	10
K/As molar ratio	1.4
weight of KTA nutrient	185 grams
target dissolution temperature	590°C
percent external fill	56%
seed orientation	(011) plates

Table VII lists the nine "large-scale" runs and shows some of the experimental variations.

### 5.2 Growth Rates

Growth rate is defined as the increase in thickness normal to the (011) seed plate and expressed as millimeters per side per week. The highest growth rate was achieved on the last run of the series at a rate of 0.77mm/sd/wk. The top seed of that run undoubtedly grew faster but it cracked due to interference from spontaneous nucleation on the wall. This growth rate compares to ~1mm/sd/wk for KTP. The growth rate increases toward the top of the autoclave since the temperature is decreasing in that direction. The exception was run 832 which had KTP seeds in the two lowest positions. The KTA overgrowth was highly strained and cracked which may have resulted in more growth hillocks.

### 5.3 Temperature and Pressure

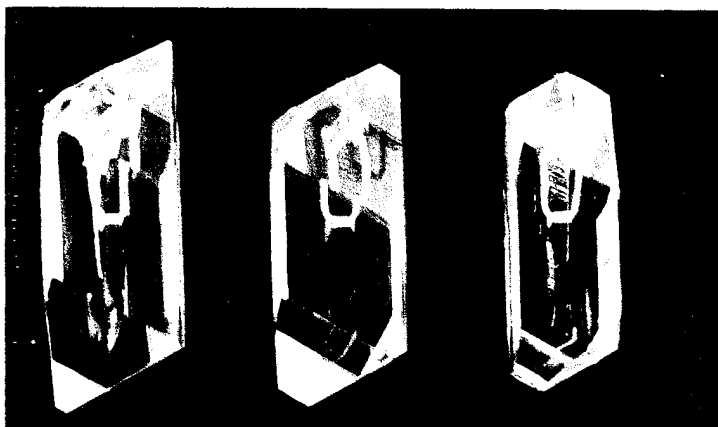
For the target nutrient or bottom temperature of 590°C the pressure should be less than 25,000psi for autoclave longevity. The initial value of internal fill of 77.5% proved to be too high. Run 830 leaked and 832 had to be limited to 563°C due to the high pressure. Subsequent runs at 73.5% internal fill produced the correct pressure. A series of three runs at 72% fill reduced the pressure to approximately 20,000psi, which after optimizing the heater temperature profile produced excellent results with run 924.

Table VII KTA Large-Scale Runs

Run #	830	832	839	846	859	872	890	915	924
System #	1	2	1	2	1	1	1	1	2
Bottom temp., °C	591	563	590	493	591	591	590	591	592
Gradient, bot-top, °C	31	39	32	31	32	31	32	32	31
% internal fill	77.5	77.5	73.5	73.5	73.5	73.5	72	72	72
Pressure, kpsi	20	26	25	25	24	25	19	19	21
Run length, days	11	60	48	4	56	54	70	70	70
Seeds (011)	2 KTA, 1 KTP	1 KTA, 2 KTP	3 KTA (DuPont)	---	3 KTA (DuPont)	KTA(flux & hydro)	3 hydro	3 hydro	3 hydro
Growth rate, top mm/sd/wk	---	.465,KTA	0.685	---	0.509	0.66	0.45	0.26	broke
Growth rate, mid mm/sd/wk	---	.622,KTP	0.678	---	0.414	0.5	0.17	0.26	0.77
Growth rate, bot mm/sd/wk	---	.508,KTP	0.528	---	0.211	0.44	0.13	0.19	0.69
Mass transport, g/day	---	2.4	2.0	---	1.6	1.7	0.3	0.3	2.0
Comments	Pressure failure	Growth temp. limited by pressure, good transport	Good run	Experimental nutrient, pressure too high	Small crystals	Small crystals	Liner leak, small brown crystals	Small crystals, colorless	Large crystals, colorless, 30grams each

## 5.4 Results

One of the relevant measurements is the mass of KTA transported per day through the baffle. From Table VII this number varied from 0.3 to 2.4 g/day. The transported material crystallizes either on the seeds or on the wall of the gold liner. A high transport rate is beneficial only if the seeded growth rate is high. For example, comparing runs 839 and 924 one sees identical mass transport but higher linear growth for 924. The high value of mass transport for run 832 was due to the higher gradient, but again the seed growth rate was relatively low. The variation in mass transport and seeded growth rate depend empirically on the power and temperature of each of the seven band heaters on the autoclave. The external temperature readings do not directly correlate with internal temperatures due to solution convection. Unfortunately, the growing crystals cannot be observed and heater power settings are iterative based on prior run history. Near the end of the contract Airtron successfully produced two nice 30 gram KTA crystals with run 924, see Figure 26. The third crystal of this run located at the top position undoubtedly grew faster than 0.77mm/side/week as measured on the middle crystal. The top crystal cracked because it was surrounded by penetrating spontaneously nucleated crystals.



Run #839

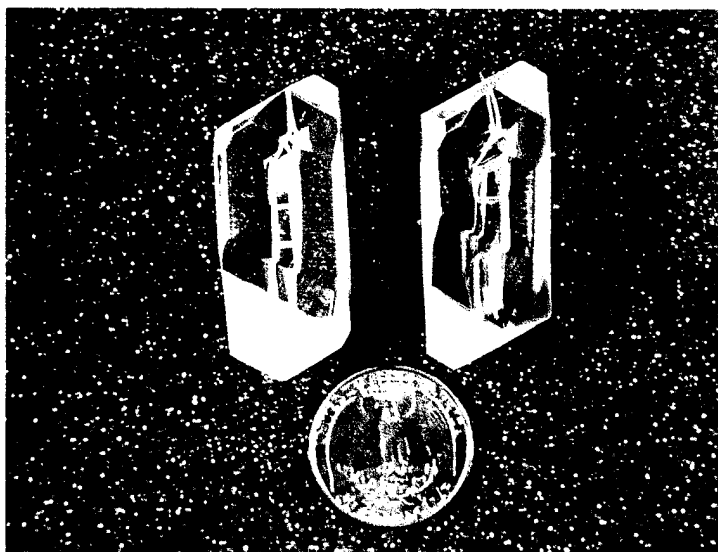


Figure 26

Hydrothermal KTA crystals

top: Run #839, typical size 12x13x28mm

bottom: Run #924, typical size 18x18x35mm



## 6.0 Crystal Quality

### 6.1 Domains

KTA crystals should be single ferroelectric domain to be usable for nonlinear optics. Early flux grown KTA was multidomain. Our hydrothermal KTA was tested at E.I. duPont Laboratories. Z-cut plates were piezoelectrically probed on a sub-millimeter scale and found to be single domain. DuPont also performed frequency doubling using a  $1.31\mu\text{m}$  fundamental, since it does not phase match at  $1.06\mu\text{m}$ . The doubled power followed a  $\text{sinc}^2x$  curve with very few side lobes, another indication that the crystals are single domain. Active testing to be reported in Section 8 also found no evidence of domains.

### 6.2 Impurity Analysis

The bottom KTA crystal from hydrothermal Run #924 was analyzed by ICP at DuPont. Nutrient for this run was grown from a tungstate-free flux. The values below represent the average of two determinations and are shown as compared to the theoretical weight percent for  $\text{KTiOAsO}_4$ :

	K %	Ti %	As %	O % by difference	P ppm	Si ppm
Measured	16.0	20.5	33.4	30.1	500	500
Calculated	16.2	19.8	31.0	33.0	0	0

The major constituents match with theory. The As may look high but the *atomic* ratio As/Ti is 1.04 which is considered within experimental error. The primary impurities detected were phosphorus and silicon. In both cases 500ppm by weight corresponds to about 0.4 atomic percent with respect to the arsenic site in the crystal.

### 6.3 Infrared Data

The substitution of As for P in the KTP structure improves the optical transmission in the 3-5 micron region. This effect was originally shown for KTA crystals grown from tungstate and molybdate fluxes<sup>29</sup>. Figure 27 shows the infrared transmission of recent KTA grown from a tungstate and molybdate free flux at DuPont. The spectrum measures unpolarized transmission through 19mm of x-axis length taken with Airtron's Perkin Elmer 1420 Infrared Spectrophotometer. The baseline transmission at  $2.5\mu\text{m}$  ( $4000\text{cm}^{-1}$ ) is arbitrary,

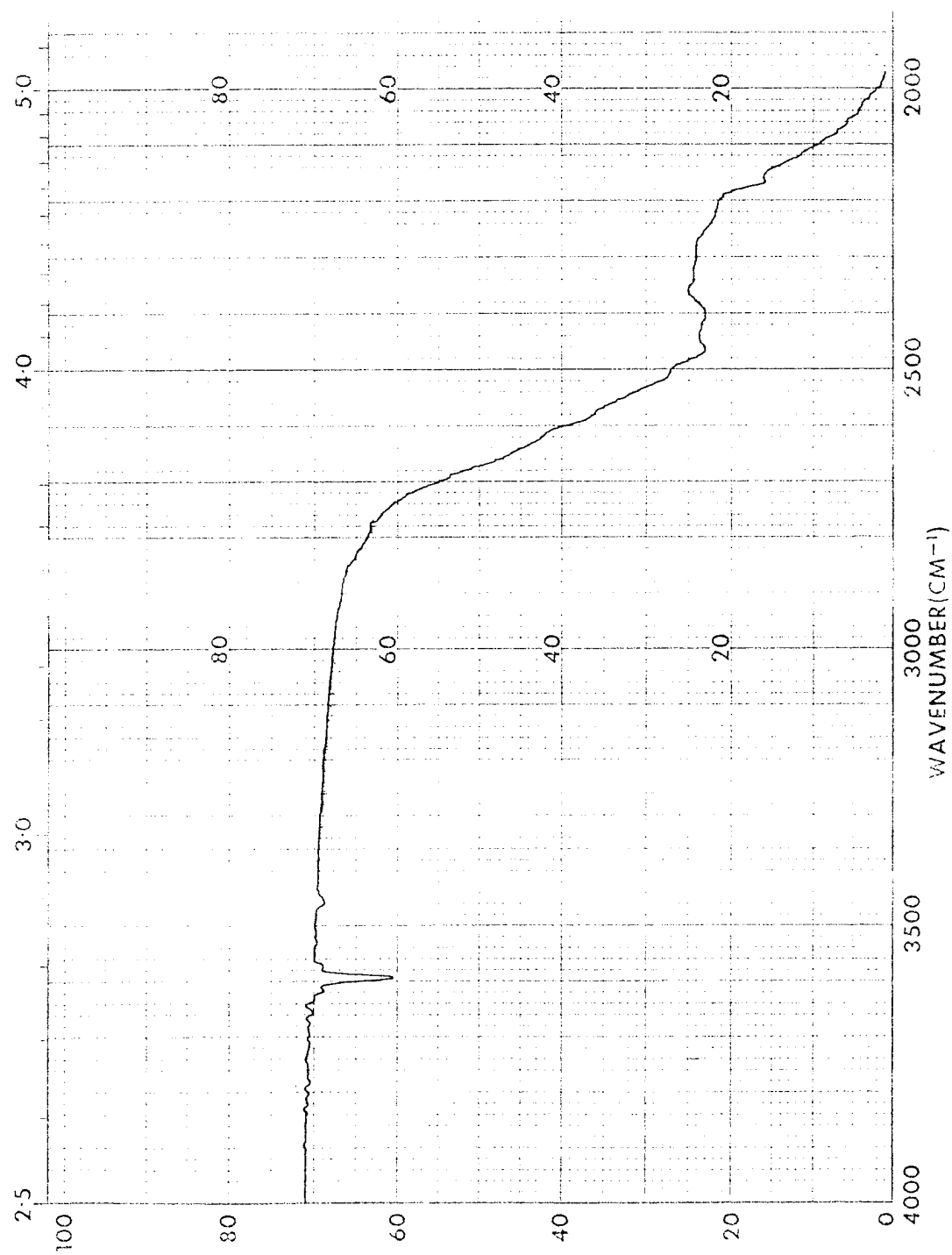


Figure 27 Infrared transmission of flux grown KTA, unpolarized, 19mm along x-axis

being determined by aperture effects. Note the small band, most likely OH, at about  $2.8\mu\text{m}$  ( $3600\text{cm}^{-1}$ ) which represents 5-10ppm OH. The flux crystal starts to absorb for wavelengths longer than about  $3.6\mu\text{m}$  ( $2800\text{cm}^{-1}$ ).

Figures 28 and 29 compare the unpolarized infrared transmission of two hydrothermal KTA runs. Figure 28 shows Run #839 through 12mm of x-axis length and Figure 29 Run #924 through 18mm along the x-axis. Note the very pronounced OH band at  $2.8\mu\text{m}$  which is characteristic of hydrothermal crystals and may represent 100-300ppm OH. OPO devices would suffer optical loss in the  $2.8\mu\text{m}$  region but the crystal quality is not affected.

These crystals also have a very broad absorption feature at about  $3.4\mu\text{m}$  ( $3000\text{cm}^{-1}$ ). The origin of the absorption remains unclear. KTP has a feature at  $3.46\mu\text{m}$  ( $2887\text{cm}^{-1}$ )<sup>29</sup> and we thought that the growth solution might have been contaminated with phosphate. However, the chemical analysis shown in Section 6.2 for crystal #924 revealed only 500ppm by weight or 0.4atomic % phosphorus, which would not be enough to explain the strength of the absorption. Also, DuPont loaned us a flux KTA crystal intentionally doped with 18% phosphorus, and it did not show this absorption. This absorption may be due to a low concentration of some unknown arsenate species incorporated under hydrothermal conditions.

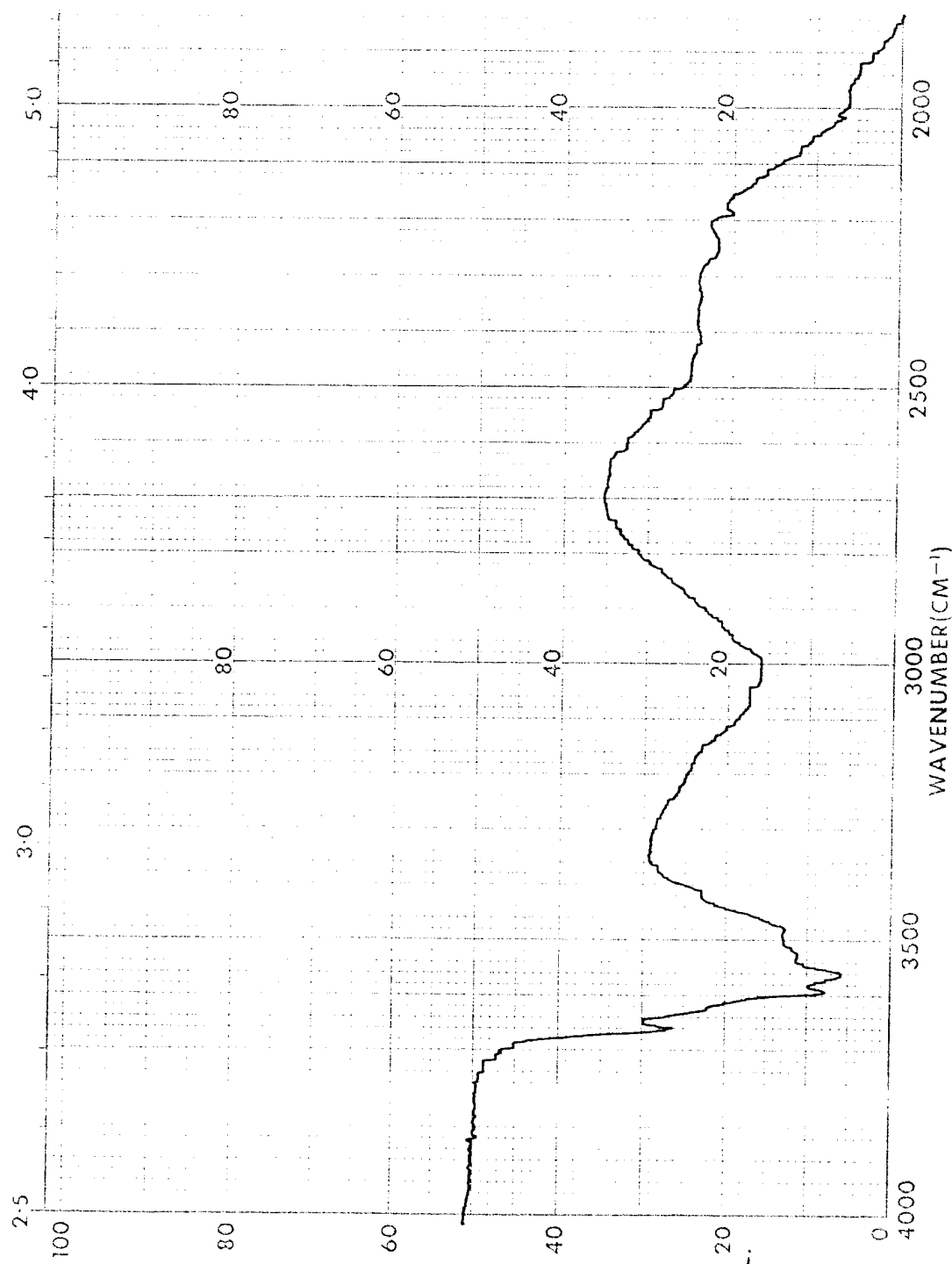


Figure 28 Infrared transmission of early hydrothermal KTA #839, unpolarized, 12mm along x-axis

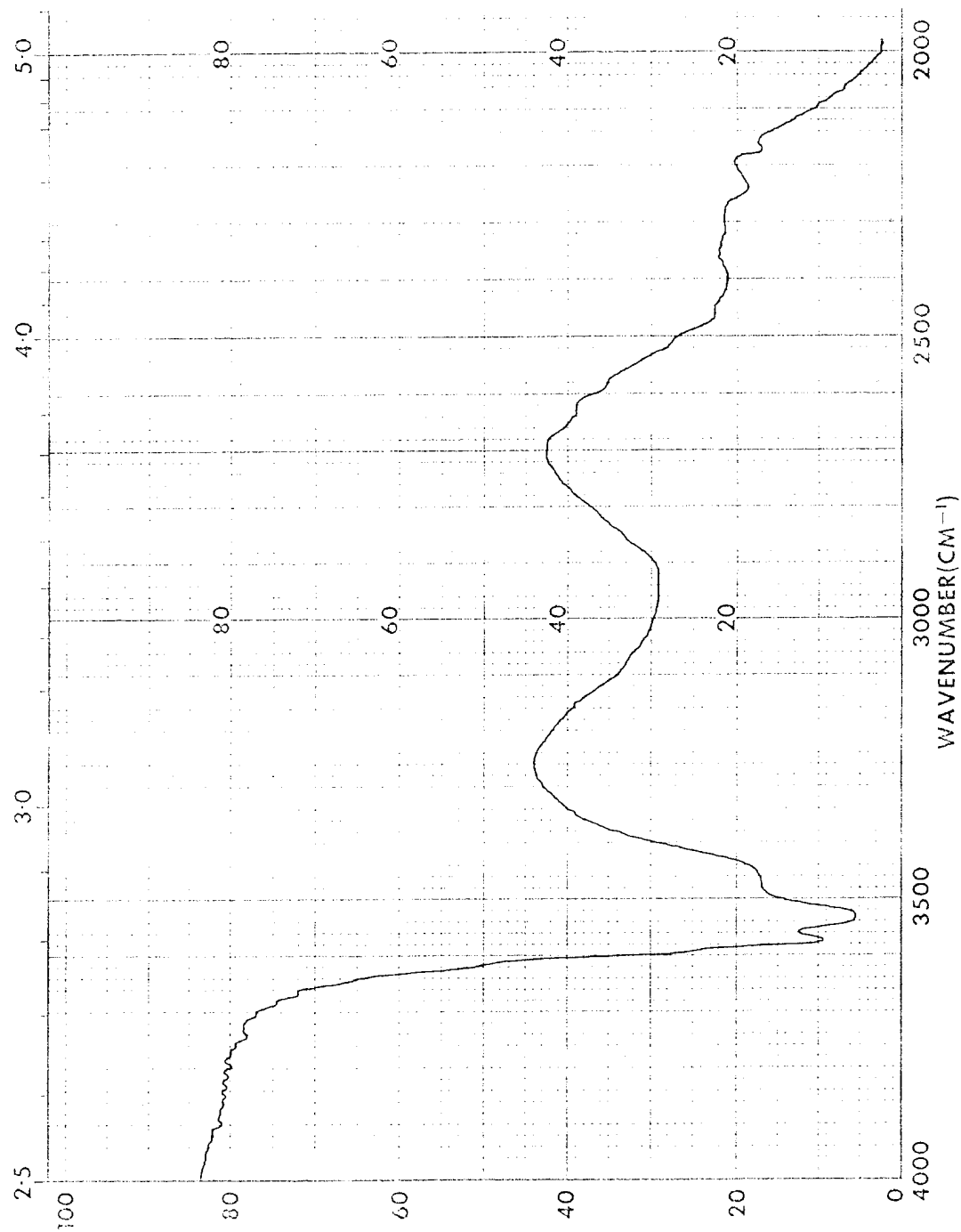


Figure 29 Infrared transmission of hydrothermal KTA #924, unpolarized, 18mm along x-axis

## 7.0 Crystal Processing

### 7.1 Orientation and Cutting

KTA like KTP has well defined facets on the as grown crystals. These serve as a convenient guide to orientation and provide accuracy within 2 degrees. More precise orientation within a few minutes of arc is obtained by using x-ray procedures based on Bragg reflection.

KTA cuts well with diamond impregnated saw blades and both inside and outside diameter types have been used. The cooling water is self contained to collect arsenic containing wastes and splash shields prevent airborne mists. Diamond grinding wheels shape the rectangular cross section and provide bevels on the sharp edges.

### 7.2 Polishing

KTA polishes similarly to KTP. After cutting and grinding to shape the parts are waxed to a glass plate and initially polished with 20 micron alumina powder. Then switching to a 9 micron powder removes work damage and the parts are mechanically brought into parallelism. The final polish is typically done with cerium oxide slurry on a flat plate.

### 7.3 Passive Testing

The finished part is inspected to a surface finish specification of 10-5 scratch-dig. The standard parallelism of the end faces is 20 arc seconds with an end face flatness of  $\lambda/4$ .

KTA sample crystals were delivered uncoated and no further passive testing was required.

## 8.0 Active Testing

The active testing of KTA is a bit of a problem because of the highly specialized equipment required. Most crystal growth is performed by companies which are not direct manufacturers of the nonlinear laser application. Nonlinear KTA was intended originally as an optical parametric oscillator crystal rather than a frequency doubling crystal. In fact, KTA cannot properly phase match the principal Nd:YAG laser line at  $1.064\text{ }\mu\text{m}$ . Because of the refractive indices of pure KTA, no phase matching can occur at fundamental wavelengths less than  $1.075\text{ }\mu\text{m}$ <sup>33</sup>. Certain impurities, such as Fe, when added to KTA<sup>7</sup>, can change the refractive indices sufficiently to obtain phase matching with  $1.064\text{ }\mu\text{m}$  sources. However, this procedure defeats the purpose of high purity since the optical damage level may be affected.

### 8.1 Internal Program

Airtron possessed sufficient equipment to actively test KTA if the application was for frequency doubling and involved laser fundamental wavelengths greater than  $1.08\text{ }\mu\text{m}$ . Thus, several solid-state laser crystal wavelengths could be used such as Nd ( $1.3\text{ }\mu\text{m}$ ), Er ( $1.5\text{ }\mu\text{m}$ ) and a few others. For doubling and parametric purposes, an extended knowledge of refractive indices must be known. Figure 30 shows a plot of data obtained at various wavelengths by the DuPont group<sup>7</sup> for hydrothermal KTA. The hydrothermal material has the same Sellmeier coefficients as high purity flux KTA. From a knowledge of the refractive index ellipsoid and the polar angles  $\theta$  and  $\phi$  measured from the z and x axes respectively, a plot of the phase matching loci can be developed. In Figure 31 we give a plot for KTA which follows that for KTP closely. Both Type I and Type II interactions are shown for phase matching around  $1.08\text{ }\mu\text{m}$ . In Figure 32 taken from Boulanger's paper<sup>33</sup>, we show SHG Type II phase matching ( $1.32\text{ }\mu\text{m}$  to  $0.66\text{ }\mu\text{m}$ ) for KTA taken from data on spheres. With this type of data, it was shown that KTA had a relative nonlinear coefficient of 1.4 times that of KTP. Thus with a Nd:YAlO<sub>3</sub> source at  $1.32\text{ }\mu\text{m}$ , ordinary frequency doubling measurements can be made on KTA and conversion efficiencies recorded for quality estimation.

### 8.2 Deliverables and Outside Testing

We had to rely primarily on research laboratories to test KTA as an optical parametric oscillator. This was necessary because commercial systems were not yet available and qualified industrial personnel were not immediately interested. For this reason, we contacted a number of capable laboratories who might test KTA. As a result of equipment availability, the required crystal size, and the particular experiment the investigator would conduct, Airtron prepared and delivered crystals according to Table VIII.

# Hydrothermally grown KTA

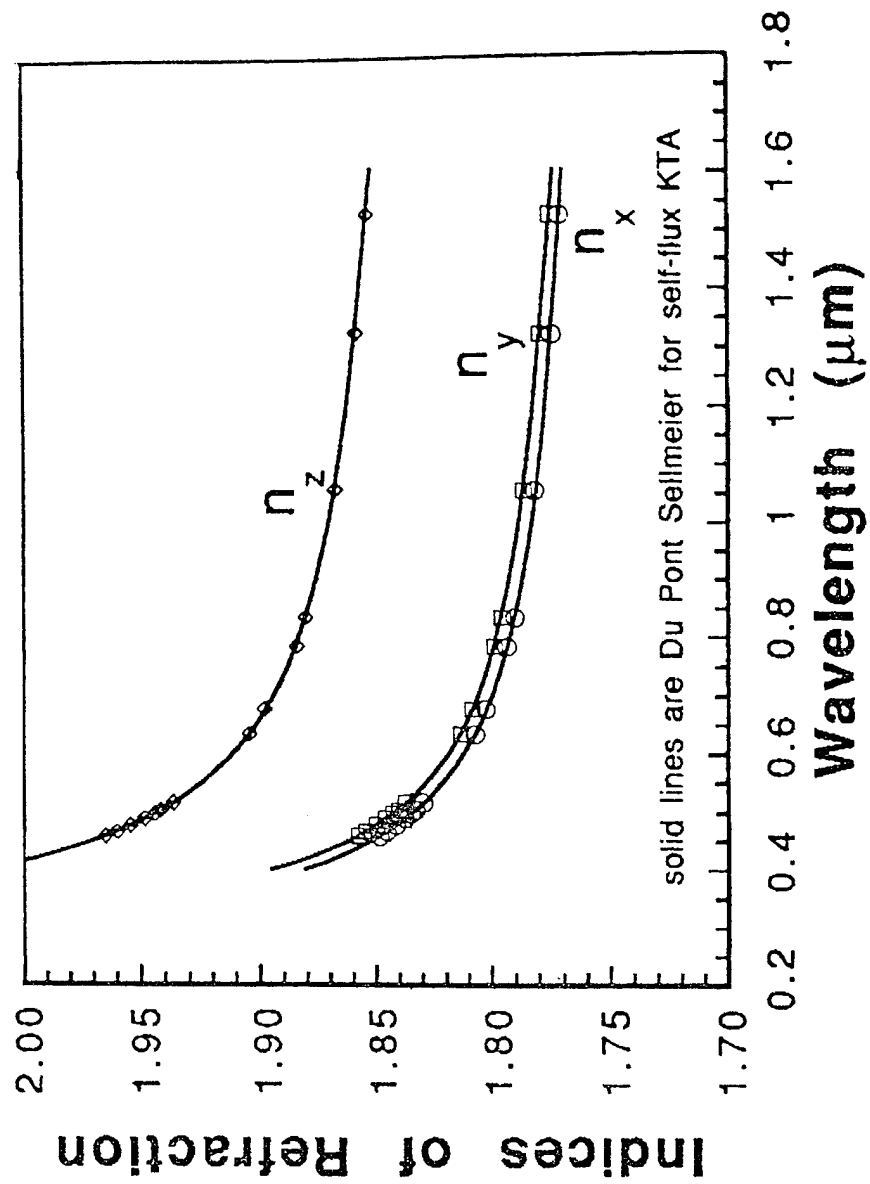


Figure 30 Hydrothermal KTA refractive indices versus wavelength



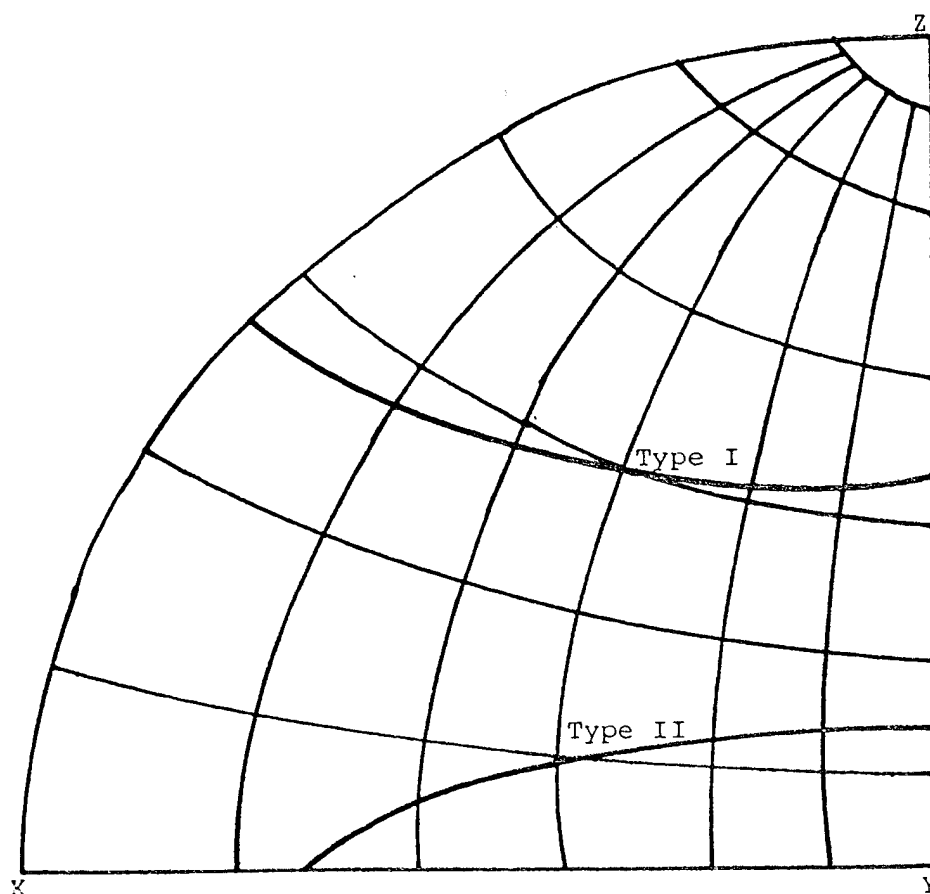


Figure 31 Stereographical plot of KTA phase matching loci <sup>33</sup>

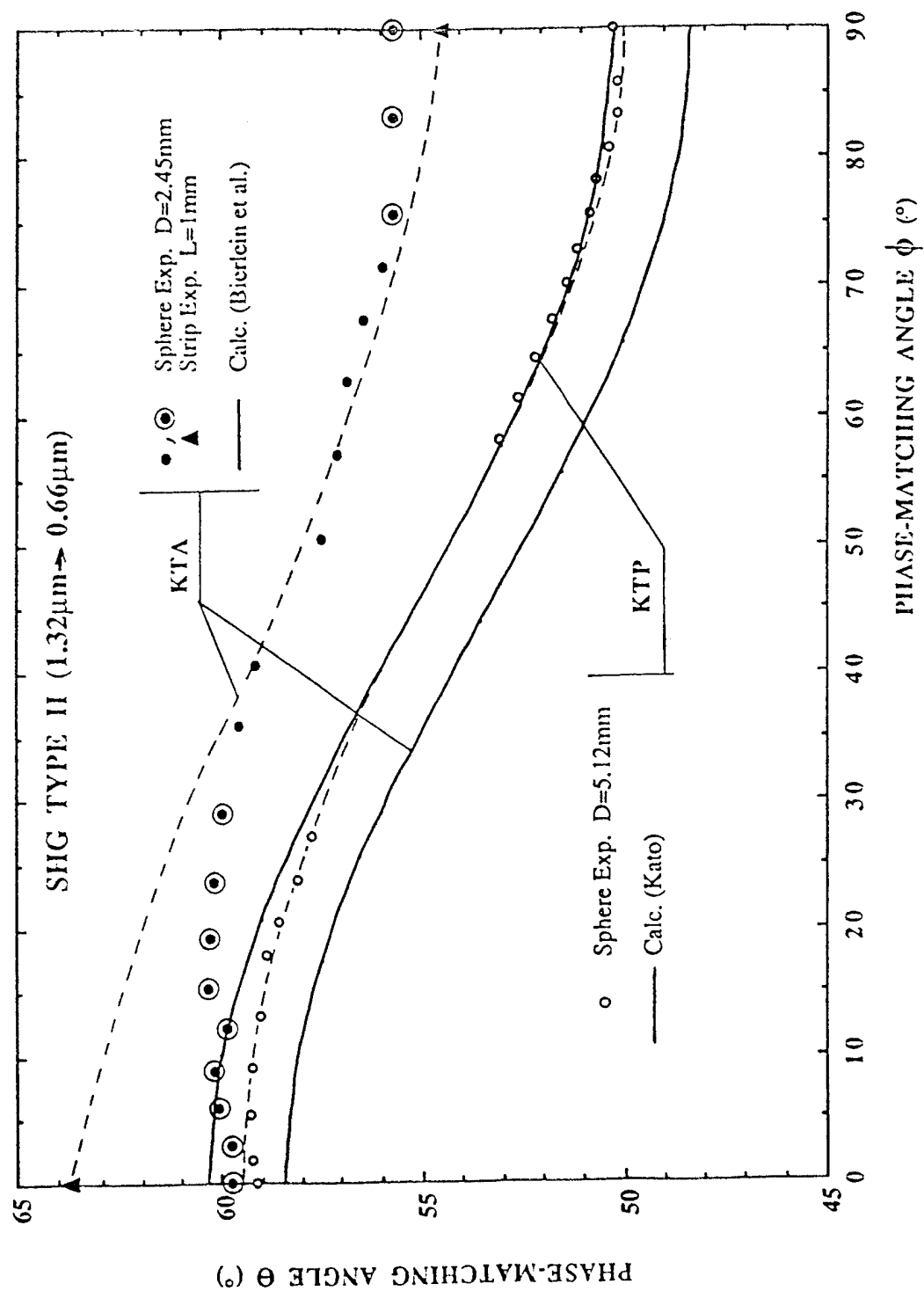


Figure 32 KTA Type II phase matching for SHG at  $1.32\mu\text{m}$ <sup>33</sup>

Table VIII KTA Test Samples Delivered

Organization	Contact	Qty	Size (mm)	Orientation $\theta$ & $\phi$	Application
U. Cal-Berkeley	Prof. Andy Kung	1	3x10x15	30°, 90°	frequency mixing
U. Cal-Berkeley	Prof. Andy Kung	1	3x10x2	30°, 90°	frequency mixing
Battelle NW Labs	Dr. Gary Holtom	2	4x4x1	90°, 0°	OPO
Battelle NW Labs	Dr. Gary Holtom	2	4x4x0.5	90°, 0°	OPO
Fibertek	Dr. Larry Marshall	3	3x3x5	90°, 0°	OPO
TRW	Dr. Eric C. Cheung	1	4x5x20	90°, 0°	OPO

### 8.3 Results

With respect to the investigators listed in Table VIII we report the following results.

Prof. Kung successfully demonstrated tunable mid-infrared OPO action from 3.0 to 5.3 $\mu\text{m}$  using difference frequency mixing<sup>34</sup>. For complete details see the published paper, the title page of which is reproduced in Appendix I. He showed 7% conversion efficiency to 4.4  $\mu\text{m}$  with 250kW peak power. He observed the broad absorption feature mentioned in Section 6.3 at "3.3 $\mu\text{m}$ ", but it did not affect his device operation. By scanning the wavelength of one of the lasers he resolved the absorption of CO<sub>2</sub> in air to less than 1cm<sup>-1</sup>.

Dr. Holtom provided unpublished results on his application which was an ultrafast OPO at 2.9-3 $\mu\text{m}$ . KTP has been tested but the longest wavelength possible with his 90fs Ti:sapphire pump was 2.7 $\mu\text{m}$ . According to the KTA Sellmeier coefficients of L.K. Cheng<sup>7</sup> the idler wavelength should be longer than KTP, but this was not found to be the case. Apparently the Sellmeier coefficients need revision. Dr. Holtom did comment that the hydrothermal KTA was of high optical quality and uniform with nonlinear coefficients "at least as large as KTP".

Dr. Marshall left Fibertek and the samples have yet to be evaluated.

Dr. Cheung measured a similar transmission curve as in our Figure 29. His OPO operates at 4 $\mu\text{m}$  which is affected by the broad absorption. He chose not to further evaluate the crystal due to the absorption.

### 8.4 KTA Property Summary

For convenient reference the properties of KTA are collected in Appendix II.

### 9.0 Deliverables

In addition to the crystals listed in Table VIII deliverables included monthly progress reports and financial data. Once or twice a year Airtron presented oral contract reviews for DARPA in Washington, DC.

## 10.0 Conclusions

This program demonstrated that good quality KTA crystals could be grown by the hydrothermal process. The solvent consisting of 12 molar  $\text{KH}_2\text{AsO}_4$  with a K / As ratio of 1.4 yields KTA crystals as the single stable phase. For an autoclave 1.5 inches inside diameter by 18 inches long with a sealed gold liner the proper pressure balancing was determined which allows growth at approximately 590°C and 25,000psi.

The growth rate on KTA seed plates oriented (011) was on the order of 1mm/side/week. A 10 week run produced 30 gram crystals of approximately 18 x 18 x 35 mm. The crystal size is typical of KTP grown hydrothermally in the same autoclave. The hydrothermal KTA was colorless and consisted of a single ferroelectric domain. Transmission spectra through 12 and 18 mm lengths of crystal showed an unexpected absorption at about 3.4 $\mu\text{m}$ . The origin of this absorption is unknown. It is postulated to be an arsenate species and may warrant further study. The absorption may introduce some loss in the 3-4  $\mu\text{m}$  region but it does not preclude OPO operation. A. H. Kung<sup>34</sup> using KTA crystals grown under this contract demonstrated continuously tunable radiation from 3.0 to 5.3 $\mu\text{m}$ .

## 11.0 Acknowledgments

The authors wish to give thanks to John Bierlein, Pat Morris Hotsenpillar and Kevin Cheng of DuPont for their help providing flux grown KTA for seeds and for nutrient. They also evaluated some of the hydrothermal crystals and coordinated chemical analysis of raw materials and crystals.

The hydrothermal KTA phase and solubility studies benefited from close cooperation with Bob Laudise of AT&T Bell Laboratories.

Airtron also acknowledges the able technical assistance of Joe Serpico and Mark Smith in the hydrothermal growth facility.

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## Hydrothermal growth of potassium titanyl arsenate (KTA) in large autoclaves

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Solubility and phase relations were investigated for selected K/As ratios in  $\text{KH}_2\text{AsO}_4$ –KOH solutions at 600°C and 2040 atm. All initial data were obtained with 5 mm diameter  $\times$  50 mm long platinum capsules in Tem-Pres type autoclaves. The most favorable results were repeated in Morey type autoclaves of 2.2 cm diameter. The  $P$ – $T$  data were generated and extrapolated for use in gold liners and René 41 autoclaves with a pressure balancing method. Transfer to the 3.8 cm diameter  $\times$  46 cm long autoclaves with gold liners was achieved. Both nutrient and larger seed crystals were grown from a  $\text{K}_2\text{WO}_4$ – $\text{Li}_2\text{WO}_4$  flux. The internal and external degrees of fill were adjusted to obtain a balance of pressure at 1700 atm and 590°C. Initial growth runs were made for 1–2 weeks under a gradient of 30°C with a 4 molar  $\text{KH}_2\text{AsO}_4$  mineralizer. Natural facet seeds were employed first while later runs utilized (011) cut and polished seeds.

### 1. Introduction

Potassium titanyl arsenate ( $\text{KTiOAsO}_4 = \text{KTA}$ ) is a nonlinear optical material with exemplary physical properties. It belongs to a class of forty compounds which are all structurally characterized by corner linked octahedrally coordinated titanium chains connected with tetrahedrally coordinated phosphorus or arsenic bridges. A good recent review of the materials and properties has been given in ref. [1]. KTA can be prepared by methods analogous to those used for  $\text{KTiOPO}_4$ . A crystal structure determination by Brahmani and Durand [2] utilized crystals grown from an arsenate self flux. The study by Hairoury et al. [3] was also done on self-fluxed crystals. Large crystals were grown from a  $\text{WO}_3$  flux to determine the nonlinear and other physical properties [4]. The flux procedure using  $\text{MoO}_3$  and  $\text{WO}_3$  was reported in detail recently [5]. Hydrothermal growth has been attempted and small crystals were obtained [6]. Most flux grown crystals contain ferroelectric domains from relatively high growth temperatures and cooling through the

880°C Curie point. The reported effective nonlinear coefficient ( $d_{\text{eff}}$ ) of KTA is 1.6 times that of KTP. This favorable property has encouraged us to undertake an examination of hydrothermal growth below 600°C.

### 2. Experimental procedure

#### 2.1. Solubility study

The first step in developing a hydrothermal growth method is to determine the solubility of the KTA in candidate mineralizer solutions. Analogous to commercially grown hydrothermal KTP [7], mixtures of  $\text{KH}_2\text{AsO}_4$  and KOH were selected as a potential mineralizers. Seed crystals of KTA were obtained by the growth of KTA from a  $\text{K}_2\text{WO}_4$ – $\text{Li}_2\text{WO}_4$  flux using the method of Ballman et al. [8]. To measure the solubility of KTA in a  $\text{KH}_2\text{AsO}_4$ –KOH– $\text{H}_2\text{O}$  mineralizer solution, a weighed seed crystal of flux grown KTA circa 0.1 g is placed in a 5 mm diameter  $\times$  50 mm long platinum capsule. The mineralizer solution



Narrowband mid-infrared generation using  $\text{KTiOAsO}_4$ 

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Continuously tunable mid-infrared radiation from 3.0 to 5.3  $\mu\text{m}$  was produced by difference frequency mixing in  $\text{KTiOAsO}_4$ . A photon efficiency of 7% for conversion to 4.4  $\mu\text{m}$  was achieved, providing peak power exceeding 250 kW, and pulse energy of over 0.5 mJ in a 2 nanosecond pulse. An absorption spectrum of  $\text{CO}_2$  in air with better than  $1\text{ cm}^{-1}$  resolution was obtained simply by scanning the wavelength of one of the input lasers.

Successful generation of continuously tunable mid-infrared (IR) radiation in  $\text{KTiOAsO}_4$  (KTA) using difference frequency mixing of an injection-seeded pulsed Ti:sapphire ring laser and a Q-switched Nd:YAG laser is reported. High power output from 3.0–5.3  $\mu\text{m}$  was obtained by tuning the injection laser from 800 to 890 nm and adjusting the phase-matching angle of the KTA crystal. Peak powers of >250 kW at 4.4  $\mu\text{m}$  and 150 kW at 5.0  $\mu\text{m}$  were achieved, corresponding to a pulse energy of 0.5 mJ and a 7% photon conversion to the mid-IR region. With modest improvements to the KTA crystal a 50% photon conversion and multimegawatt IR power that has transform-limited spectral resolution should be possible.

The mid-infrared region of 3.0–5.3  $\mu\text{m}$  is of particular significance for molecular spectroscopy, infrared photochemistry, and atmospheric sensing applications. Many important molecules have strong transitions spanning this spectral region. For many years there have been many attempts to obtain an efficient high power infrared laser source that will cover this entire region in a single package. However, this has not been achieved, primarily due to a lack of suitable optical materials. Nonlinear crystals such as  $\text{LiNbO}_3$  (Ref. 1) and  $\text{KTiOPO}_4$  (Ref. 2) (KTP) have now established durability and high optical quality. Yet their usefulness is limited to wavelengths shorter than 4.4  $\mu\text{m}$  because of intrinsic absorption in the material. Single crystals of  $\text{AgGaS}_2$ ,  $\text{AgGaSe}_2$ , and  $\text{ZnGeP}_2$  were used for parametric generation at longer wavelengths.<sup>3–7</sup> However, these ternary chalcopyrite crystals either have low optical damage threshold for repeated operation<sup>5</sup> or required the use of a mid-infrared (1.5–2  $\mu\text{m}$ ) laser as pump source.<sup>7</sup> Furthermore, broadly tunable narrowband operation with these crystals has yet to be reported. The crystal KTA is an isomorph of KTP and has optical properties very similar to those of KTP.<sup>8</sup> Unlike KTP, however, KTA has optical transmission that spans from the ultraviolet (UV) at 0.35  $\mu\text{m}$  to the IR beyond 5.3  $\mu\text{m}$ . This makes KTA particularly attractive for mid-IR generation. Recently, large single domain KTA crystals are successfully produced using both the flux technique<sup>9</sup> and the hydrothermal growth technique.<sup>10</sup> Refractive index measurements show that the crystal is phase matchable for parametric generation up to its absorption edge at 5.3  $\mu\text{m}$ . Parametric oscillation in the 1.5  $\mu\text{m}$  region with flux-grown material have been reported for nanosecond<sup>11</sup> and femtosecond operation.<sup>12</sup> The present letter reports direct generation of narrowband 3.0–5.3  $\mu\text{m}$  radiation using hydrothermally grown KTA by parametric mix-

ing of a single-frequency tunable Ti:sapphire laser and a pulsed Nd:YAG laser.

Parametric mixing or difference frequency mixing (DFG) can be a very effective approach to generating narrowband infrared radiation. While optical parametric oscillators (OPO) are relatively simple to build, implementing good linewidth control that is often required for practical devices necessarily increases the OPO oscillation threshold, sometimes to a prohibitively high value and at the very least reduces the OPO efficiency substantially.<sup>13</sup> In the case of IR generation, rapid falloff in parametric gain due to the longer wavelength makes narrowband OPOs very difficult to become practical. DFG, on the other hand, involves the use of two near-IR 0.8–1.0  $\mu\text{m}$  lasers which are well developed and reliable. The near-IR wavelengths can be controlled to a very high degree of precision and stability. In this approach, the only requirement is to identify a nonlinear crystal that has good optical quality and is robust enough to provide sustained long-term operation.

The KTA crystal used in this experiment is provided by Litton/Airtron Synoptics. It is one of the first single domain KTA crystals that was successfully grown using the hydrothermal growth method. The advantage of this method, as demonstrated by KTP,<sup>14</sup> is high damage threshold, good crystal uniformity, and low ionic conductivity. These are factors that are critical for efficient DFG operation. Theoretically, in order to maximize the nonlinearity and thus the conversion efficiency, the crystal should be cut for type II phase matching in the  $xz$  plane ( $\varphi=0^\circ$ ,  $\theta=40^\circ$ ).<sup>11</sup> In practice the size of currently grown boules has limited the dimensions of a finished crystal to  $4\times 4\times 2$  mm long if it was cut in this orientation. On the other hand, IR phase matching is also possible for propagation in the  $yz$  plane ( $\varphi=90^\circ$ ) at  $\theta\approx 30^\circ$ . Since this is close to the natural growth direction of the crystal, comparatively large crystal sizes can easily be obtained. A comparison of the figure of merit,  $d_{\text{eff}}^2/(d_{\text{eff}} l)$  (the effective second order nonlinearity in question and  $l$  is the crystal length), shows that, given the constrain on the size of presently available crystals, propagation in the  $yz$  plane will be a factor of 10.5 more effective for DFG than propagation in the  $xz$  plane. The crystal was therefore cut at  $\varphi=90^\circ$ ,  $\theta=30^\circ$ . Its finished size was  $10\times 2.7\times 15$  mm<sup>3</sup>. This crystal has a slightly pale color, but is free of inclusions, and shows refractive index striations along the 15 mm length near the center portion of the crystal. These striations are caused by the seed crystal near which the present crystal was cut. Nev-

## Appendix II: KTA Physical Properties

PROPERTY	VALUE	Reference
Composition	KTiOAsO <sub>4</sub>	
Crystal structure	orthorhombic mm2	5
Space group	Pna2 <sub>1</sub>	5
Lattice constants		
a <sub>0</sub> , b <sub>0</sub> , c <sub>0</sub> Angstrom	13.125, 6.5716, 10.786	29
Density, g/cm <sup>3</sup>	3.454	29
Refractive index, from Sellmeier equation @ 1064nm		
n <sub>x</sub>	1.7811	32
n <sub>y</sub>	1.7866	
n <sub>z</sub>	1.8518	
Transparency, nm	350-5300	29
Nonlinear optical coefficients, pm/V @ 1064nm		
d <sub>31</sub>	2.8	7
d <sub>32</sub>	4.2	7
d <sub>33</sub>	16.2	7
d <sub>24</sub>	10.8	30
d <sub>15</sub>	6.0	30
Phase matching range, nm		
Type II SHG, x-y plane	1075-1134	31
Electrooptic coefficients, pm/V		
r <sub>13</sub>	11.5	32
r <sub>23</sub>	15.4	
r <sub>33</sub>	37.5	
Dielectric constant, low frequency		
ε <sub>33</sub>	18	5
ε <sub>11</sub> = ε <sub>22</sub>	12	
Curie temperature, °C	880	5